American Mineralogist, Volume 87, pages 562–565, 2002

Reidite: An impact-produced high-pressure polymorph of zircon found in marine sediments

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ABSTRACT

Reidite is a high-pressure polymorph of zircon with the scheelite structure. It has been found in an upper Eocene impact ejecta layer in marine sediments on the upper continental slope off New Jersey and on Barbados. Reidite occurs (epitaxially oriented) in shock-metamorphosed zircons. It is associated with impact glass (tektites), shocked quartz and feldspar with multiple sets of planar deformation features, coesite, and trace amounts of stishovite. This phase was first produced in high-pressure laboratory experiments in 1969 and has also been produced in shock recovery experiments. Reidite is brittle with an irregular fracture, a hardness of 7.5, a calculated density of 5.2 g/cm^3, a white streak, adamantine luster, and it does not fluoresce. In index oil in transmitted light, shocked zircon grains consisting almost entirely of reidite are transparent. Pleochroism was not observed. Reidite appears to have parallel extinction and is length slow. The maximum birefringence is roughly 0.015. Reidite appears to be uniaxial positive. It is tetragonal, space group $I4_1/a$, $a = 4.738$ (1) Å, $c = 10.506$ (2) Å, $V = 235.84(2)$ Å^3. Previous shock-loading experiments on zircons indicate that the transition to reidite starts at about 30 GPa and is completed around 53 GPa. Reidite should be a useful indicator of peak pressure in shock metamorphosed rocks. Reidite is named after Alan Reid who first produced this phase in the laboratory.

INTRODUCTION

While documenting shock effects in zircon grains recovered from an impact ejecta layer found in upper Eocene sediments on the upper continental slope off New Jersey, we discovered that some of the more heavily shocked grains contain a high-pressure polymorph of zircon. We have named this new mineral reidite after Alan F. Reid who first produced this phase (a high-pressure zircon polymorph with the scheelite structure) in high-pressure laboratory experiments in 1969 (Reid and Ringwood 1969). This species and name have been approved by the international Mineralogical Association Commission on New Minerals and Mineral Names. Holotype material is deposited at the Smithsonian Institution (National Museum of Natural History), Washington, D.C., catalog number NMNH 173504.

OCCURRENCE

The shocked zircon grains containing reidite were recovered (Glass and Liu 2001) from an impact ejecta layer found at three sites on the upper continental slope off New Jersey: Deep Sea Drilling Project Site 612, Ocean Drilling Program (ODP) Hole 903C, and ODP Hole 904A (Table 1) (Thein 1987; Glass 1989; Glass and Wu 1993; Glass et al. 1998). More recently, several shocked zircons containing reidite have been found in what is believed to be the same ejecta layer on the island of Barbados. The ejecta at all of these sites are believed to have come from the 90 km diameter Chesapeake Bay impact structure found at the mouth of the Chesapeake Bay (Poag et al. 1994; Koeberl et al. 1996).

At sites 612 and 904A, the impact ejecta layer consists primarily of impact glass (tektite fragments and microtektites), quartz, feldspar, and rock fragments exhibiting various degrees of shock metamorphism. Some of the quartz and feldspar have multiple sets of planar deformation features and some of the quartz grains have been partly to completely converted to coesite (Glass 1989; Glass et al. 1998). Traces of stishovite have also been documented. Some of the glass and silicate grains are coated with, and in some cases partly replaced by, pyrite. Glauconite is also abundant in the layer. The ejecta layer also contains some microfossils, primarily foraminifera and radiolaria. The ejecta layer at Site 903C is similar to that found at the other two sites except that no impact glass is present. The heavy mineral assemblage at all three sites is similar and consists of Fe and Ti oxides (grains probably consisting of mixtures of ilmenorutile and ilmentite), garnet (mostly Fe-rich), staurolite, rutile, epidote, ilmenite, zircon, titanite, Al_2SiO_5 phases (including kyanite), and tourmaline, in approximate order of decreasing abundance.

PHYSICAL AND OPTICAL PROPERTIES

The shocked zircon grains containing reidite make up about 23% of the zircons recovered from the ejecta layer, and they range up to 80 × 200 × 200 μm in size. The size of the reidite crystals is difficult to determine. However, scanning electron

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microscope images of a shocked reidite-bearing zircon grain, etched in a saturated solution of NaOH at 70 °C for 1.5 h, show a brighter phase that stands out in relief relative to the bulk of the grain. We assume that this phase is reidite. It appears to have the same composition as the zircon, but the crystals are too small to analyze. The reidite consists of elongate skeletal crystals up to 10 μm in length and 0.3 μm in width (Fig. 1). The orientation of the elongate crystals appears to be controlled by crystallographic directions within the host zircon. This interpretation is supported by the observations of Leroux et al. (1999), who produced this high-pressure zircon polymorph in shock-recovery experiments (they referred to it as the scheelite structure phase). They studied the shocked zircon by transmission electron microscopy and electron diffraction and found thin bands (0.1 to several micrometers in width) of the scheelite structure phase.

Shocked zircon grains consisting almost entirely of reidite (based on X-ray diffraction patterns, see below) are white opaque in reflected light and have an adamantine luster. When viewed in transmitted light (in an index oil), the grains are transparent with a pale brownish-green color. We did not observe any evidence of cleavage.

The reidite domains in the shocked zircon grains are too small to allow determination of most of the physical properties. However, we obtained some larger grains consisting almost entirely of the high-pressure zircon polymorph with a scheelite structure (i.e., reidite) that were produced in shock recovery experiments (Fiske et al. 1994). The artificially produced reidite is white when powdered. It is brittle with an irregular fracture and has a Mohs hardness of ~7.5. The naturally shocked zircons consisting almost entirely of reidite show no fluorescence under long-wave or short-wave ultraviolet light. Reid and Ringwood (1969) calculated that the high-pressure zircon polymorph (reidite) is 11% denser than zircon, based on unit-cell size, which indicates a density of ~5.2 g/cm^3.

TABLE 1. Sample locations

Site	Core	Section	Depth (cm)	N. Lat.	W. Long.
DSDP 612	21×	5	111–114	38.82	72.78
ODP 903C	56×	6	25–27	38.94	72.82
ODP 904A	45×	2	84–86	38.86	72.77
Bath Cliff, Barbados			13.20	59.51	

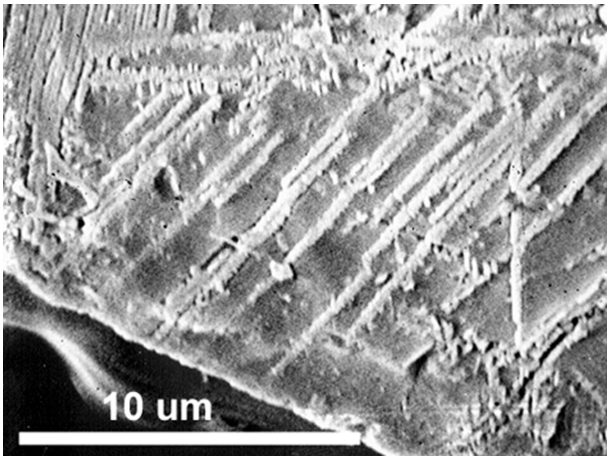

FIGURE 1. Scanning electron microscope photomicrograph of the surface of an etched shocked zircon with a skeletal crystalline phase that may be reidite. X-ray diffraction data indicate that this zircon contains minor amounts of reidite.

A naturally shocked zircon grain consisting almost entirely of reidite exhibited no pleochroism. The grain has parallel extinction and is length slow. The inferred maximum birefringence is roughly 0.015. The grain appears to be uniaxial. The sign could not be determined, but is inferred to be positive since the grain is length slow. The indices of refraction are >>1.64.

Reidite appears to be epitaxially oriented with respect to the precursor zircon. Kusaba et al. (1986) used X-ray powder diffraction data to determine the structural parameters of the scheelite phase. They concluded that during shock-induced transformation, the [110] direction of zircon is converted to the [001] direction of the scheelite phase (reidite). Based on a transmission electron microscopic study of experimentally shocked zircon, Leroux et al. (1999) found that the (112) plane of the scheelite phase(reidite) is parallel to the (100) plane of the zircon structure, and the [110] direction of the scheelite phase (reidite) is parallel to the [001] direction of the zircon structure.

COMPOSITION

Electron microprobe analysis of a shocked zircon containing mostly reidite (from the upper Eocene impact ejecta layer) indicates that reidite has a composition similar to zircon (Table 2). The empirically derived formula, based on four O atoms, is $(Zr_{1.01}Hf_{0.01})Si_{0.99}O_4$. The simplified formula is $(ZrHf)SiO_4$. Reidite produced in other impact events can have different compositions depending on the compositions of the pre-shock zircons.

CRYSTALLOGRAPHY

Powder diffraction patterns were obtained for several shocked zircons using a Gandolfi camera with Ni-filtered Cu$K\alpha$ X-radiation. The pattern reported in Table 3 was scanned and digitized using the Filmscan software program and the Jade 3.1 computer program was used to determine the *d*-spacings and intensities (Table 3). We observed all but four of the weaker lines reported by Liu (1979) for the high-pressure zircon polymorph with a scheelite structure (Liu produced this phase in high-pressure laboratory experiments). Several of the stronger

TABLE 2. Composition of shocked zircon composed primarily of reidite determined by electron microprobe analysis*

	SiO_2	ZrO_2	HfO_2	TiO_2	FeO	Al_2O_3	MgO	Total
	31.82	66.47	1.22	0.05	0.03	0.00	0.08	99.67
	31.80	66.55	1.23	0.05	0.06	0.02	0.07	99.78
	32.10	65.78	1.25	0.06	0.06	0.01	0.07	99.33
	30.70	64.87	1.33	0.05	0.21	0.02	0.13	97.21
	30.76	65.91	1.22	0.07	0.10	0.01	0.10	98.17
Avg.	31.44	65.92	1.25	0.06	0.09	0.01	0.09	98.86

* The accelerating voltage was 15 kV and the beam current was 40 nA. A minimum beam diameter was used. SI zircon standard was used for Zr, Hf, and Si; bytownite was used for Al; Kakanui hornblende was used for Mg and Ti. No Y or Ca was detected.

TABLE 3. X-ray diffraction data for reidite and artificially produced reidite (scheelite-type $ZrSiO_4$), and zircon for comparison

Observed*				Scheelite-type $ZrSiO_4$†				Zircon	
Visual‡		Digitized§			Obs.	Cal.		PDF no. 6-0266	
d (Å)	*I*	*d* (Å)	*I*	*hkl*	*d* (Å)ǁ	*d* (Å)	*I*	*d* (Å)	*I*
		4.469	4					4.43	45
4.30	40	4.309	30	101	4.30	4.30	25		
3.29	40	3.301	7					3.30	100
3.18	<10								
2.94	10								
2.81	100	2.823	100	112	2.811	2.809	100		
						2.801			
2.61	20	2.628	10	004	2.616	2.613	15		
2.51	20	2.525	5					2.518	45
2.36	20	2.369	7	200	2.360	2.356	15		
2.2	<10							2.217	8
2.065	50	2.076	19	211	2.067	2.066	20	2.066	20
					2.03	2.056	<5		
1.91	15	1.919	7	105	1.913	1.911	15	1.908	14
1.805	30	1.813	11	213	1.806	1.803	15		
1.755	60	1.760	18	204	1.754	1.750	20	1.751	12
1.71	20							1.712	40
1.675	10	1.677	17	220	1.668	1.666	15		
1.65	<10							1.651	14
1.55	45	1.554	14	116	1.546	1.553	15	1.547	4
						1.544			
1.48	<10	1.487	3					1.477	8
1.437	50	1.441	17	132	1.437	1.433	20		
1.41	10	1.413	5	224	1.407	1.405	10		
1.38	<<10							1.381	10
1.315	<<10				1.30	1.306	<5		
						1.297			
1.255	<<10				1.26	1.256	<5	1.259	8
1.22	<<10				1.22	1.224	<5		
						1.218			
1.185	<10				1.178	1.178	5		
1.14	15	1.148	4	208	1.142	1.142	5		
					1.131	1.132	10		
1.11	<10	1.140	7	411	1.11	1.108	<5		
1.08	<<10	1.062	3	420	1.086	1.086	10		
					1.073	1.074	10		
1.058	<<10	1.035	3	228	1.053	1.054	10	1.059	8
					1.026	1.027	<5		
1.00	<10				1.003	1.003	<5		
					0.9964	0.9971	<5		
0.982	<10	0.9841	4	424	0.9808	0.9833	15		

* Pattern of a shocked zircon from ODP Site 904 obtained using a Gandolfi camera (115 mm diameter) with Cu$K\alpha$ radiation with a Ni filter.

† Liu 1979.

‡ Spacings were determined visually using a template and intensities were estimated visually.

§ The pattern was scanned and digitized and a computer program was then used to determine the *d*-spacings and intensities.

ǁ Measurements made with a modified 57.3 mm Debye-Scherrer camera using Co$K\alpha$ radiation.

lines for zircon were also present in this pattern (Table 3). Some of the weaker lines did not match lines for either the high-pressure zircon polymorph (reidite) or zircon. The Jade 3.1 computer program was used to calculate the cell parameters: $a = 4.738(1)$ Å, $c = 10.506(2)$ Å, and $V = 235.84(2)$ Å^3. These values are similar to values given by previous workers based on studies of this phase produced in laboratory experiments (e.g., Liu 1979; Kusaba et al. 1985).

Reidite is isostructural with scheelite and is tetragonal with space group $I4_1/a$ (Reid and Ringwood 1969), based on analogy with scheelite. Si is in tetrahedral coordination with O. Infrared spectra indicate that the Si-O configurations do not differ between reidite and zircon (Kusaba et al. 1985). Zr is in eightfold coordination, more regular in reidite than in zircon, with four equal Zr-O bonds and four more of slightly greatly length (Reid and Ringwood 1969). Infrared spectra confirm a difference in Zr-O configuration between reidite and zircon (Kusaba et al. 1985). Silica is believed to totally occupy the tetrahedral sites and Zr the eightfold sites.

Previous crystallographic studies of the high-pressure zircon polymorph with a scheelite structure made in laboratory experiments have shown that reidite is formed from zircon by a displacive (martensitic-like) transformation (Kusaba et al. 1985, 1986; Leroux et al. 1999).

FORMATION CONDITIONS

Shock-loading experiments on zircons by Kusaba et al. (1985) indicate that transition to reidite (the scheelite structure) starts at about 30 GPa and is completed around 53 GPa. Above about 90 GPa, $ZrSiO_4$ begins to decompose into ZrO_2 and SiO_2 (Kusaba et al. 1985). Fiske et al. (1994) were able to produce 1–2% scheelite phase by shock compression of zircon at 20 GPa, 10–15% at 30 GPa, and 100% at 52 GPa. Thus our shocked zircons that now consist primarily of reidite were probably shocked between 50 and 90 GPa.

USE AS AN INDICATOR OF PEAK SHOCK PRESSURE

Several authors have predicted that the high-pressure $ZrSiO_4$ scheelite phase (reidite) should be found in naturally shocked rocks (e.g., Kusaba et al. 1985; Fiske et al. 1994; Leroux et al. 1999). Stishovite is presently being used as a diagnostic mineralogical criterion of impact despite that the fact the kinetics of the quartz-to-stishovite transition are slow and stishovite reverts to an amorphous phase at temperatures as low as 300 °C. Zircon, on the other hand, transforms fully under shock loading and the high-pressure polymorph survives to a much higher temperature (up to 1000 °C) than does stishovite (Fiske et al. 1994). In addition, zircon is much more refractory and resistant to alteration than most other minerals. Furthermore, zircon can be dated by the U-Pb method and thus provide additional information about the provenance of the target rocks as well as the time of the impact (e.g., Schärer and Deutsch 1990; Krogh et al. 1993; Kamo and Krogh 1995). Thus, reidite should be useful as an indicator of peak shock pressure in shock metamorphosed rocks.

ACKNOWLEDGMENTS

We thank T. Nagase for help with X-ray diffraction studies and scanning electron microscopy. T. Rose of the Analytical Laboratories, Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution, performed the electron microprobe analysis. The Ocean Drilling Program provided the core samples. We also thank P.S. Fiske for providing samples of the high-pressure zircon polymorph with scheelite structure (reidite) produced in shock recovery experiments. This research was supported by NSF grant EAR-9903811 to B.P.G.

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MANUSCRIPT RECEIVED AUGUST 27, 2001
MANUSCRIPT ACCEPTED DECEMBER 11, 2001
MANUSCRIPT HANDLED BY ALISON R. PAWLEY