LETTER

Akaogiite: An ultra-dense polymorph of TiO$_2$ with the baddeleyite-type structure, in shocked garnet gneiss from the Ries Crater, Germany

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ABSTRACT

Akaogiite, an ultra-dense polymorph of TiO$_2$ was encountered in heavily shocked garnet-cordierite-sillimanite gneiss in the Suevite breccia of the Ries meteorite impact crater in Germany. The chemical formula of akaogiite is TiO$_2$, containing (wt%) TiO$_2$ 97.6–97.7; Nb$_2$O$_5$ 0.15–0.20, and FeO 0.11–0.14. The empirical formula is: Ti$_{0.998}$Fe$_{0.002}$Nb$_{0.001}$O$_2$. Akaogiite is optically distinguishable from rutile only in reflected light microscopy, through its slightly higher brightness and the intense royal blue color of its internal reflections in crossed nicols. The mineral grains consist of countless randomly oriented submicrometer particles. In situ micro-beam X-ray diffraction established akaogiite to be monoclinic with the baddeleyite-type structure. Cell parameters are a = 4.606(2) Å, b = 4.896(3) Å, c = 4.933(3) Å, and β = 99.17(6)°; space group $P2_1/c$; molar volume = 16.82(2) cm^3/mol; density = 4.72 g/cm^3. Akaogiite coexists in the shocked gneiss with graphite-diamond phase transition assemblage, a second dense TiO$_2$ polymorph with the scrutinyite-type structure (TiO$_2$-II), liquidus idiomorphic jadeite inclusions in melt pockets in garnet, and a new FeTiO$_3$-polymorph with the Li-niobate structure. The high-pressure assemblage constrains the equilibrium peak-shock pressure to be ≤22 GPa and a post-shock temperature <500 °C, thus correcting previous estimates. The name was approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2007-058). The name is for Masaki Akaogi, Professor at the Department of Chemistry, Gakushuin University in Tokyo, Japan.

Keywords: Akaogiite, Ries Crater, suevite impact breccia, shock, rutile, TiO$_2$-II, graphite, diamond, Li-niobate structured FeTiO$_3$

INTRODUCTION

The Ries Crater in Germany was first established as a meteorite impact site in 1961 and further confirmed in 1963 through the discovery of the high-pressure polymorphs of silica, coesite, and stishovite, in the shocked crystalline rocks of the crater by E.C.T. Chao and his colleagues (Shoemaker and Chao 1960, 1961; Chao and Littler 1962, 1963). In situ studies of carbon phases in the same gneiss clasts revealed the presence of the graphite-diamond phase transition (El Goresy et al. 2001b). That study unraveled details of the intrinsic settings and microscopic textures of graphite and diamond supporting the solid-state inversion mechanism. It also uncovered diamond to secondary graphite back transformation that took place after decompression. Such information is usually lost during extraction of shock-induced coesite, stishovite (Stöffler 1971), and diamond through chemical demineralization techniques (e.g., Koeberl et al. 1997) that separate mineral constituents, causing the entire loss of the

parental low-pressure phases and erasure of the phase transformation textures. We advocate that the various shock-induced phase transformations are better studied through in situ petrographic investigations and not chemical separation techniques. We here document the mineralogical and the crystallographic nature of akaogiite concisely described before (El Goresy et al. 2001a), and present new constraints on the equilibrium shock pressure and post-shock temperature responsible for the rutile to akaogiite phase transition and its preservation.

This mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association as a new mineral with the name akaogiite on February 3, 2008 (IMA 2007-058). The name is in honor of the eminent mineral physicist Masaki Akaogi for his seminal contributions to experimental petrology, calorimetry, and mineralogy, including experimental characterization of high-pressure polymorphs of TiO$_2$ relevant to planetary deep interiors. The type material (El Goresy section No. BGI 3) has been deposited in the collection of the Bayerisches Geoinstitut, Universität Bayreuth, Germany.

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PHYSICAL PROPERTIES

We investigated several polished thin sections of shocked graphite-diamond-bearing gneiss from the suevite localities of Altebürg inside the Ries crater, Otting and Seelbronn east of the crater rim. Rock slices were impregnated in vacuum with Crystal Bond epoxy prior to grinding and polishing to fill and seal original cracks, shock-induced fractures, and keep disaggregated mineral grains together.

Akaogiite occurs within multiphase TiO$_2$ clusters enclosed in biotite in the shocked gneisses (Fig. 1). Streak, luster, hardness, tenacity, cleavage, fracture, density, possible twinning, pleochroism, anisotropy, and reflectivity values in reflected light were not determined because of the polycrystalline nature of the grains and the submicrometer size of the individual crystallites. The density calculated from the empirical formula is 4.72 g/cm^3. The polycrystalline akaogiite grains are bright white in reflected polarized light. Akaogiite can be easily recognized and located within shocked rutile clusters only in reflected light and crossed polars (Fig. 1) through its intense royal blue internal reflections, in contrast to the white internal reflections of rutile and to the brown to pink internal reflections of TiO$_2$-II, respectively. Aka-

ogiite also exhibits blue fluorescence under the electron beam like both rutile and TiO$_2$-II. The mineral is extremely sensitive to any laser or focused electron beam irradiation and it inverts in seconds to rutile. For this reason we failed to collect a Raman spectrum of akaogiite even using low laser power below 5 mW. Prolonged X-ray irradiation also induces inversion back to rutile ≤12 h.

OCCURRENCE AND ASSOCIATED MINERALS

Akaogiite occurs in the shocked gneiss in clusters of three TiO$_2$ polymorphs either with or without ilmenite, titanite, and graphite. The three TiO$_2$ polymorphs: rutile, TiO$_2$-II, and akaogiite have a distinct spatial arrangement: akaogiite occupies in many rutile clusters their cores and is surrounded either by rutile grains (or by TiO$_2$-II followed by an outer belt of rutile). The close proximity of the three polymorphs within a distance of less than 200 µm strongly advocates for higher thermal stress during the shock pulse in the interior of the original rutile clusters rather than for a variable magnitude of the pressure pulse within grains of the same shock impedance as previously and incorrectly suggested by El Goresy et al. (2001a) to be the controlling factor. Garnet in the gneiss clast depicts sieve texture with numerous silica and plagioclase feldspar pockets that melted at high pressure and subsequently quenched before decompression. The inclusions contain quenched melt pockets mainly consisting of dense silica glass. Some of the melt inclusions host liquidus idiomorphic jadeite crystals up to 5 µm in length. The gneiss also contains the new natural Li-niobate structured polymorph of FeTiO$_3$ (Dubrovinsky et al. 2009).

CRYSTAL STRUCTURE AND CHEMICAL COMPOSITION

A 140 µm assemblage consisting of akaogiite, rutile, and ilmenite and containing a 120 µm akaogiite grain in its center [Figs. 1a and 1b in El Goresy et al. (2001a)] was cleanly extracted from the polished thin section using a high-precision micro-drilling instrument. The single-grain X-ray investigations were conducted with a Bruker X-ray diffractometer at the Institute of Earth Sciences, Uppsala University, Sweden. Details of the procedure and results are given in (El Goresy et al. 2001a). That study revealed an X-ray pattern convincingly matching that of the experimentally synthesized, monoclinic, high-pressure TiO$_2$ polymorph with the baddeleyite-type ($P2_1/c$) structure. The complete X-ray diffraction pattern and the d-spacings of all measured X-ray reflections are given in (El Goresy et al. 2001a). The four strongest X-ray reflections have the d-spacings: 2.929, 2.626, 2.437, and 1.686 Å, respectively.

Chemical analyses were carried out with an ARL-SEMQ electron-probe microanalyzer (EMPA) using wavelength dispersive techniques and single-channel analyzers to inhibit X-ray interferences. Operating conditions were 15 kV excitation voltage and a sample current of 10 nA with a defocused 5 µm beam to reduce the electron beam damage. Standards used were synthetic rutile (99.99 wt% TiO$_2$), synthetic fayalite, and synthetic Nb$_2$O$_5$. Matrix corrections were made by standard procedures (Bence and Albee 1968; Albee and Ray 1970). The chemical formula of akaogiite is TiO$_2$, containing (wt%) TiO$_2$ 97.6–97.7; Nb$_2$O$_5$ 0.15–0.20, and FeO 0.11–0.14.
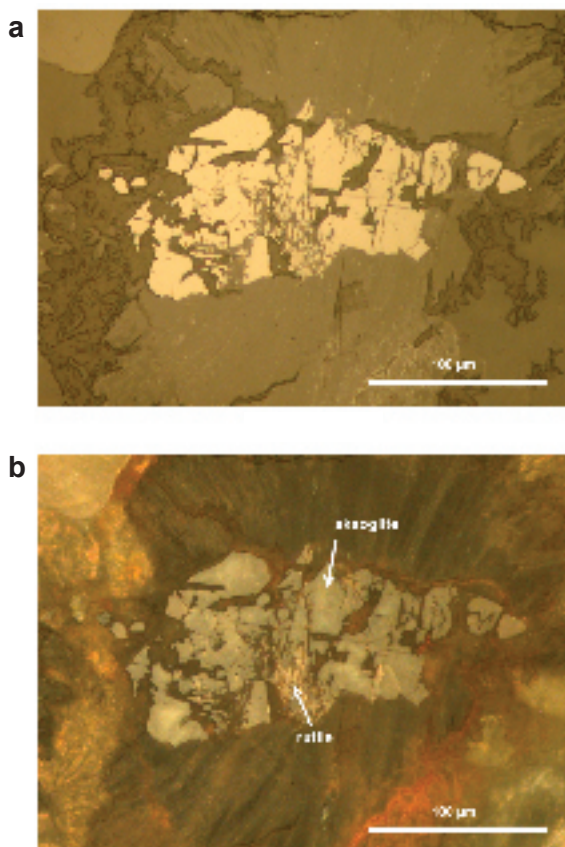

FIGURE 1. A reflected-light photographs, displaying an aggregate of akaogiite grains. (**a**) Plane polarized light. Almost all grains are akaogiite. Needles in the central part are rutile. (**b**) With crossed polars. The material with blue internal reflections is akaogiite. The rutile needles in the central part have white internal reflections.

DISCUSSION AND ORIGIN

The textural setting of the three TiO$_2$ polymorphs is quite remarkable, since it reveals information on the possible conditions of the rutile-akaogiite and rutile-TiO$_2$-II phase transformations [Figs. 2a and 2b in El Goresy et al. (2001a); El Goresy et al. (2001c)]. A strong variation of the magnitude of the equilibrium peak-pressure by more than 10–15 GPa in the core of the clusters as previously suggested by El Goresy et al. (2001a) seems unlikely because it appears unrealistic to assume a large variation in the magnitude of the equilibrium peak-shock pressure within only a few tens of micrometers among the same mineral grains with originally the same density. The microscopic settings of akaogiite in the cores of the clusters, surrounded outward by TiO$_2$-II or rutile or both, rather advocates for the increase in the thermal stress, whereas the shock temperature was highest in its more tightly packed interior, and the pressure just at or slightly ≤22 GPa. The partial melting of some garnet grains and their quenching to a fine-grained wormy garnet symplectite is additional evidence for localized high temperatures, thus inducing localized heating and thermal stress in the neighboring assemblages (Holland and Carpenter 1986). The neighboring sillimanite does not show any sign of dissociation or melting (Atou et al. 2007). It exhibits lower birefringence and planar deformation features. The lack of dissociation of the liquidus jadeite inclusions in the melt pockets in garnet to stishovite + Ca-ferrite may entirely exclude the possibility that the pressure only slightly exceeded its 22 GPa upper bound (Kubo et al. 2010). However, the jadeite crystallized from the shock-induced silicate melt, which functions as a perfect pressure-transmitting medium, hence we consider a pressure overstepping of only a few GPa beyond 22 GPa to be unlikely. We maintain, that if the equilibrium shock-pressure should have overstepped the 22 GPa upper bound of the jadeite stability prior to its crystallization from the melt, the liquid would have crystallized Ca-ferrite-structured NaAlSiO$_4$ + stishovite instead of large idiomorphic crystals of jadeite. A recent experimental study (Kubo et al. 2010) demonstrated that the solid-state nucleation of the Ca-ferrite phase in its stability field is quite sluggish in that the solid-state dissociation of jadeite to stishovite + Ca-ferrite could not develop within the short duration of the shock event. However, jadeite in the melt pockets within garnet crystallized from silicate melts in which cation diffusion should be several orders of magnitude faster than in solids. In any case, the growth rate of a liquidus crystal cannot be higher than the diffusion rate of its cations in the silicate melt (Langenhorst and Poirier 2000). Consequently, the liquidus jadeite probably crystallized at or just below 22 GPa.

The equilibrium peak-shock pressure can be better constrained than suggested earlier (El Goresy et al. 2001a) through the coexistence of both the Li-niobate-structured polymorph of ilmenite that formed through inversion from the perovskite polymorph during decompression at $P > 20$ GPa (Ross et al. 1989; Dubrovinsky et al. 2009; Wu et al. in review), and the lack of any evidence for the Ca-ferrite-structured NaAlSiO$_4$ polymorph and stishovite assemblage instead of the liquidus jadeite. Our new analysis demonstrates that the equilibrium peak shock-pressure was definitely below the experimentally determined upper bound for the ZrO$_2$-structured polymorph at 28 GPa (Dubrovinskaia et al. 2001) and can be more tightly constrained to ≤22 GPa at ≥1000 °C. This is the tightest estimate ever achieved for any shocked crystalline rock from the Ries suevite or other impact ejecta. This is in contrast to a span of 14–28 GPa estimated earlier by (El Goresy et al. 2001a). The post-shock temperature at the observed TiO$_2$ cluster cannot have exceeded 500 °C (Linde and DeCarli 1969). These authors experimentally demonstrated that TiO$_2$-II is unstable above this temperature at ambient pressure and inverts in laboratory time-scale to rutile. This orthorhombic dense polymorph occurs at the outer rims of rutile crystals and would not have survived in such a setting at higher post-shock temperatures. However, we maintain, that the post-shock temperature of the TiO$_2$ clusters cannot have reached the 500 °C thermal upper bound of TiO$_2$-II either, in view of the extreme thermal metastability of akaogiite, which otherwise would have inverted back to polycrystalline rutile in a short time at higher temperature.

Dubrovinskaia et al. (2001) and Dubrovinsky et al. (2001) reported that the molar volume of experimentally synthesized baddeleyite-structured TiO$_2$ is $V_0 = 16.90(3)$ cm^3/mol. This value (16.90 cm^3/mol) is confirmed in the recent report by Al-Khatabeh et al. (2009). In comparison, (El Goresy et al. 2001a) calculated a V_0 of natural akaogiite of only 16.82(2) cm^3/mol. These authors suggested that natural akaogiite in the studied garnet gneiss probably did not invert back to rutile either due to the existence of intrinsic post-shock residual stress in akaogiite of about 1.5 GPa and/or the presence of minor elements (0.14 wt% FeO and 0.20 wt% Nb$_2$O$_5$). They advocated that the suggested residual stress may have stabilized the structure after decompression and prevented its inversion back to rutile for 15 Ma. The V_0 values reported by Swamy et al. (2005, 2009) were obtained through diamond anvil experimental investigations conducted at room temperatures on nanocrystalline TiO$_2$ powder, which may have yielded different molar volumes as compared to the bulk TiO$_2$.

The chemical analyses totaled to 98.09 wt% with an apparent deficit of 1.91 wt%. No elements, other than those measured, were detected during energy dispersive studies using the SEM or with the wavelength dispersive technique in the EMPA. We explain the shortage of 1.91 wt% in the analyses totals as due to unevenness of the polished surface of the polycrystalline akaogiite grain during the studies. Further analytical attempts would have destroyed the crystal structure of the type specimen and inverted it to rutile without any compositional change.

All Ti measured by EPMA in akaogiite was calculated as Ti^{4+}, however, we cannot exclude the possibility of some Ti^{3+}. The presence of the characteristic royal blue internal reflections of akaogiite in crossed polars (El Goresy et al. 2001a) as also shown in Figure 1b strongly suggests the presence of some amount of Ti^{3+}.

The discovery of akaogiite and the associated diverse high-pressure polymorphs offers a unique possibility to constrain the equilibrium shock pressure and the magnitude of the post-shock temperature. Thus, we demonstrate the importance of and need for applying P-T equilibrium parameters of all coexisting high-pressure polymorphs. Other estimates obtained from measurements of the refractive indices of diaplectic glasses (Stöffler 1972, 1974) are less reliable because the refractive indices and densities of the diaplectic glasses were established at their

closure temperatures of relaxation after decompression and hence have no relevance to the magnitude of the equilibrium shock pressures, shock temperatures, or post-shock temperatures responsible for their amorphization.

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