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Qingsongite, natural cubic boron nitride: The first boron mineral from the Earth's mantle

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Abstract

Qingsongite (IMA 2013-30) is the natural analog of cubic boron nitride (c-BN), which is widely used as an abrasive under the name "Borazon." The mineral is named for Qingsong Fang (1939–2010), who found the first diamond in the Luobusa chromitite. Qingsongite occurs in a rock fragment less than 1 mm across extracted from chromitite in deposit 31, Luobusa ophiolite, Yarlung Zangbu suture, southern Tibet at 29°13.86N and 92°11.41E. Five electron microprobe analyses gave B 48.54 ± 0.65 wt% (range 47.90–49.2 wt%); N 51.46 ± 0.65 wt% (range 52.10–50.8 wt%), corresponding to $B_{1.113}N_{0.887}$ and $B_{1.087}N_{0.913}$, for maximum and minimum B contents, respectively (based on 2 atoms per formula unit); no other elements that could substitute for B or N were detected. Crystallographic data on qingsongite obtained using fast Fourier transforms gave cubic symmetry, $a = 3.61 \pm 0.045$ Å. The density calculated for the mean composition $B_{1.100}N_{0.900}$ is 3.46 g/cm^3, i.e., qingsongite is nearly identical to synthetic c-BN. The synthetic analog has the sphalerite structure, space group $F\bar{4}3m$. Mohs hardness of the synthetic analog is between 9 and 10; its cleavage is {011}. Qingsongite forms isolated anhedral single crystals up to 1 μm in size in the marginal zone of the fragment; this zone consists of ~45 modal% coesite, ~15% kyanite, and ~40% amorphous material. Qingsongite is enclosed in kyanite, coesite, or in osbornite; other associated phases include native Fe; TiO_2 II, a high-pressure polymorph of rutile with the αPbO_2 structure; boron carbide of unknown stoichiometry; and amorphous carbon. Coesite forms prisms several tens of micrometers long, but is polycrystalline, and thus interpreted to be pseudomorphic after stishovite. Associated minerals constrain the estimated pressure to 10–15 GPa assuming temperature was about 1300 °C. Our proposed scenario for formation of qingsongite begins with a pelitic rock fragment that was subducted to mid-mantle depths where crustal B originally present in mica or clay combined with mantle N ($\delta^{15}N = -10.4 \pm 3‰$ in osbornite) and subsequently exhumed by entrainment in chromitite. The presence of qingsongite has implications for understanding the recycling of crustal material back to the Earth's mantle since boron, an essential constituent of qingsongite, is potentially an ideal tracer of material from Earth's surface.

Keywords: Cubic boron nitride, deep mantle, crustal boron, mantle nitrogen

Introduction

Boron is quintessentially an element of the Earth's upper continental crust, as the crust is markedly enriched in B (17 ppm B, Rudnick and Gao 2005) relative to primitive mantle (0.26 ppm B, Palme and O'Neill 2005) and CI chondrite (0.775 ppm B, Lodders 2010). Leeman and Sisson (2002) concluded that the transfer of boron from the mantle to the crust is "essentially unidirectional," that is little, if any, boron is returned to the mantle, even in deeply subducted crust, and thus the concentration of B in the upper continental crust is expected to increase with the passage of time. A corollary of this concentration is that none of the 262 valid minerals in the IMA list known to contain essential B (http://rruff.info/ima/) has been reported either in mantle rocks or in meteorites; all are found in rocks of clearly crustal origin and many are water soluble compounds found at or near the Earth's surface.

A possible exception to this distribution is cubic boron nitride, c-BN, which Dobrzhinetskaya et al. (2009) reported from a kyanite-coesite-bearing silicate assemblage rimming a core of Fe-Ti alloy in a rock fragment less than 1 mm across extracted from chromitite in deposit 31, Luobusa ophiolite, Yarlung Zangbu suture, southern Tibet at 29°13.86N and 92°11.41E (Fig. 1), and now approved as the new mineral qingsongite (IMA 2013-30, Dobrzhinetskaya et al. 2013). Cubic-BN (c-BN) was synthesized for the first time in 1957 by General Electric Co.

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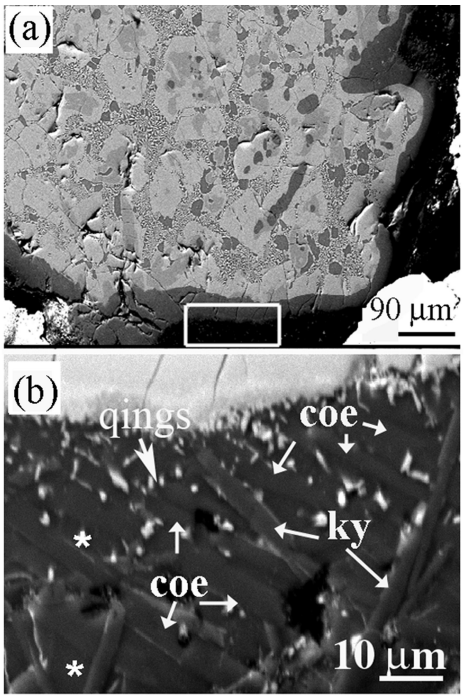

Figure 1. Scanning electron microscope images of the rock sample containing qingsongite (from Dobrzhinetskaya et al. 2009). (**a**) Backscattered electron image of Fe–Ti pellet rimmed by silicate rock (boxed area). (**b**) Detail of the boxed area shows silicate material containing coesite (coe), kyanite (ky), qings (qingsongite), unknown amorphous phase (*) of the composition: (SiO_2 = 63.00, Al_2O_3 =14.50, TiO_2 = 9.02, CaO = 0.5, MgO = 4.26, K_2O = 5.16, in wt%), and osbornite (bright spots).

from hexagonal boron nitride (h-BN) in the presence of metal solvent catalysts (Wentorf 1957, 1961). Synthetic c-BN is isostructural with sphalerite (Solozhenko et al. 1990; Eichhorn et al. 1991), which in the industrial literature is referred to as "zincblende"; i.e., c-BN has cubic closest-packing and is a homeotype of diamond. Synthetic c-BN is second only to diamond in hardness (Gardinier 1988), and thus has found wide use as an abrasive material under the trade name "Borazon"; it also has potential applications in electronics and ceramics (Wentorf 1957, 1961; Vel et al. 1991; Haubner et al. 2002; Horvath-Bordon et al. 2006). Earlier it was thought that synthesis of stable c-BN can be performed only at high pressures and high temperatures (e.g., >40 GPa, >1200 °C, Corrigan and Bundy 1975), but further experimental and theoretical studies reported successful synthesis at relatively low pressures and temperatures, e.g., at 1.5–2.0 GPa and 500–700 °C in supercritical hydrazine, N_2H_4, with Li_3N as an additive (Demazeau et al. 1995). Nonetheless, because catalysis, nucleation, and solvents play major roles in c-BN synthesis (e.g., Wang et al. 2004), the stability of c-BN relative to other BN polymorphs such as h-BN, rhombohedral BN (r-BN), and wurtzite-structured BN (w-BN) polymorphs are still controversial.

In considering the origin of qingsongite, leading questions are not only the conditions of formation, which can be constrained by stability field of its host mineral (coesite pseudomorphous after stishovite), but also the source of boron and nitrogen for a mineral formed at a depth estimated to be at least 300 km (Dobrzhinetskaya et al. 2009). The only B concentrations exceeding 1 ppm in minerals from mantle depths are reported in type IIb blue diamonds (1–8 ppm B, N < 5–10 ppm, Gaillou et al. 2012), and it is thought that B in diamonds could have been sourced from the crust. In general, nitrogen impurities are widespread in kimberlitic-lamproitic diamond and abundances can range three orders of magnitude depending on the source of the diamond (e.g., a few parts per million to over 1000 ppm, Palot et al. 2012); diamonds from ultrahigh-pressure metamorphic terrains contain up to 11 000 ppm N (Dobrzhinetskaya et al. 2010).

Mineral name and type material

The c-BN mineral and its name qingsongite have been approved by the Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association (IMA 2013-30) (Dobrzhinetskaya et al. 2013). It had been included in the list of Valid Unnamed Minerals (Smith and Nickel 2007) as UM2009-32-N:B-BN (boron nitride). The mineral was named in honor of Qingsong Fang (1939–2010), Professor at the Institute of Geology, Chinese Academy of Geological Sciences, who found the first diamond in the Luobusa chromitite in the late 1970s, and contributed to the discovery of four new species: yarlongite, zangboite, qusongite, and luobusaite in the Luobusa ophiolite. Type material is deposited in the collections of the Geological Museum of China, 15 Yangrouhutong, Xisi, West District, Beijing 100034, PR China, catalog number M 11843.

Appearance, physical and optical properties

Qingsongite forms isolated anhedral single crystals from 100 nm up to 1 μm in size. Because qingsongite is a nanomineral that occurs in quantities far too small for characterization of the physical and optical properties readily measured in larger samples, we have cited measurements on the synthetic analog. Mohs hardness of the synthetic analog is between 9 and 10; its cleavage is {011} (Gardinier 1988). The calculated density is 3.46 g/cm^3 assuming the average composition $B_{1.100}N_{0.900}$ and cell parameter of 3.61 Å; densities reported for synthetic analogs are 3.488(3) g/cm^3 (Soma et al. 1974) and 3.487 g/cm^3 (Eichhorn et al. 1991). Synthetic c-BN is colorless, but impurities can render it yellow, orange, or black (Haubner et al. 2002; Wang et al. 2003). Refractive index at 589.3 nm (sodium light) is estimated to be 2.117 in the synthetic analog (Gielisse et al. 1967).

Chemical composition

Energy-dispersive (ED) X-ray analysis was used to determine chemical composition (Figs. 2a and 2b). Spectra were acquired with a JEOL JXA-8900 Super Probe and with a transmission electron microscope (Technai-F20 XTWIN) operating at 200 kV with a field emission electron source in the scanning transmission mode (STEM) by using the TIA software package for data evaluation. TEM foils were prepared with a FEI focus ion beam (FIB) device. Significant mass loss during analysis with the TEM was avoided by scanning the beam in a preselected window (according to the size of the measured volume). Spot size was 1 nm, and acquisition time was 60 s.

The EDX spectra show only boron (B) and nitrogen (N); no

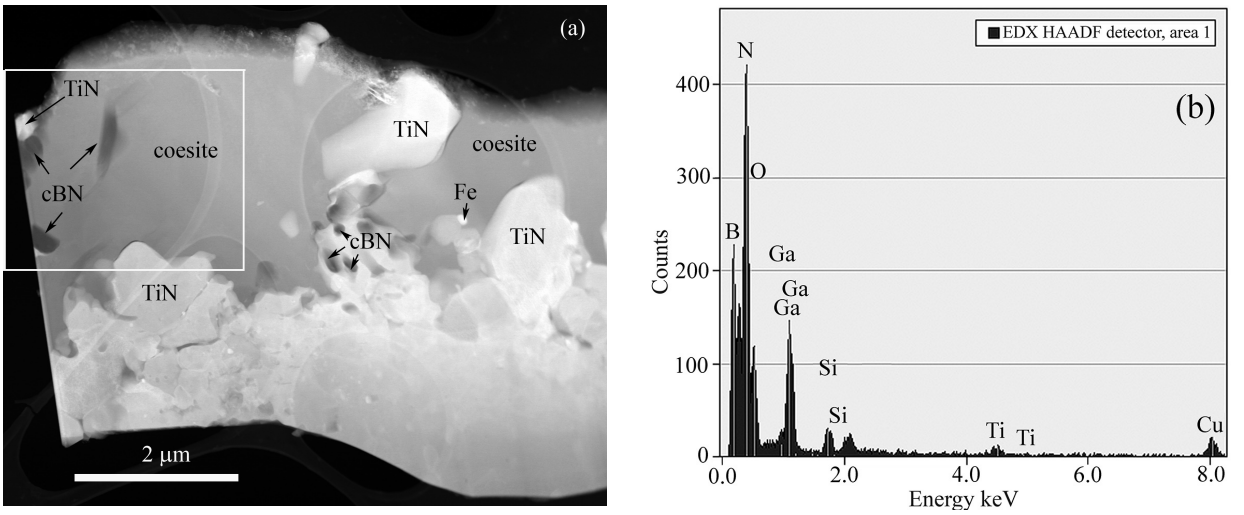

Figure 2. (**a**) A part of the TEM foil exhibits coesite matrix (light gray contrast), osbornite (TiN, bright contrast), qingsongite (c-BN, darker gray contrast) (modified from Dobrzhinetskaya et al. 2009). (**b**) Energy-dispersive X-ray spectrum shows presence of intense peaks for boron = B and nitrogen = N (inclusion of qingsongite) considering the small fluorescence yields of boron and nitrogen. Ga-peak originates from Ga-implantation during the TEM foil preparation with FIB; Cu X-ray intensity is from the TEM Cu-grid; Si and O X-ray intensities are from matrix coesite; and Ti is from neighboring osbornite.

other element that could substitute for B or N, e.g., C, was detected (Fig. 2b). The Si, O, Ti, Cu, and Ga X-ray photon intensities in the spectra originated from the host coesite, osbornite, Cu-grid and from gallium implanted during FIB milling, respectively. No carbon coating was applied to the FIB-foils, and therefore we exclude the possibility that boron was misidentified as carbon, because the peaks are resolved in EDX spectra (C*K*α = 0.277 keV and B*K*α = 0.183 keV).

The presence of both boron and nitrogen and the absence of carbon in each measured crystal of qingsongite were additionally verified with electron energy loss spectroscopy (EELS), which gave a 1:1 atomic ratio (Figs. 3a and 3b). Element mapping of the boxed area shown on Figure 2a clearly indicates that the areas for B, N, and Ti corresponding to c-BN and TiN (Figs. 4a–d) do not overlap with the area of silicon and oxygen (Figs. 4e and 4f) corresponding to coesite.

The chemical composition of qingsongite was also measured with a JEOL JXA-8900 Super Probe electron microprobe in the wavelength-dispersive spectroscopic (WDS) mode at 15 kV accelerating potential and 20 nA probe current, a 1 μm beam size and a counting period of 10 s. Quantitative analyses were carried out without standards using the $\phi(\rho Z)$ method for correction (JEOL Ltd 1993-handouts); the 1σ error of measurements is 2%. Five analyses gave B 48.54 ± 0.65 wt% (range = 47.90–49.2 wt%); N 51.46 ± 0.65 wt% (range 52.10–50.8 wt%), whereas stoichiometric c-BN has the composition of 43.6 wt% B and 56.4 wt% N. Formulas calculated from the maximum B and minimum N, and minimum B and maximum N contents gave $B_{1.113}N_{0.887}$ and $B_{1.087}N_{0.913}$, respectively, suggesting excess of boron not detected in the EELS. Excess boron has also been reported in synthetic c-BN, i.e., analysis of the first synthesis gave $B_{1.035}N_{0.965}$ (Wentorf 1957). Black color in synthetic c-BN has been attributed to excess B (Wentorf 1961; Haubner et al. 2002; Bogdanov 2008). Bogdanov's (2008) detailed study showed that extra B atoms can be incorporated in c-BN, resulting not only in an increase in the lattice parameter *a*, as had been reported by Lawaetz (1972), but also in a distortion of the structure. Thus, excess B in natural c-BN is plausible, but more precise and better calibrated chemical analysis would be needed to determine whether non-stoichiometry is real and not merely an artifact of the analytical method.

Crystallography

Crystallographic data on qingsongite were obtained with the Technai-F20 XTWIN instrument operating at 200 kV using a field emission electron source. Fast Fourier transforms (FFT) were calculated from high-resolution lattice fringe images by measuring the lengths of the different vectors displayed in the diffraction patterns (Fig. 5). The FFT were calibrated with graphite that is present in the same foil and an external albite standard: the standard deviation was 0.06 Å for 10 measurements in albite. In addition, we used Pt that was deposited on the top of the foil prior to FIB sputtering as internal standards for calibrating the qingsongite lattice parameter (Table 1). Our calculations gave a lattice parameter of 3.61 Å for qingsongite. We have calculated that the average of absolute values of the differences between measured and literature values for d_{hkl} is 0.045 Å, and that the standard deviation is 0.046 Å (Table 1).Given this standard deviation, our cell parameter is consistent with cell parameters reported for synthetic c-BN, which range from 3.6150 to 3.6160 Å with uncertainties between 0.001 and 0.0001 Å (Wentorf 1957; Soma et al. 1974; Will et al. 1986; Eichhorn et al. 1991; Solozhenko et al. 1990).

The correct indexing of the diffraction patterns as c-BN was re-checked by comparing the observed angles between corresponding vectors in the diffraction patterns with the angles between adjacent planes from literature data. Additionally, we calculated the angles between adjacent planes in the diffraction

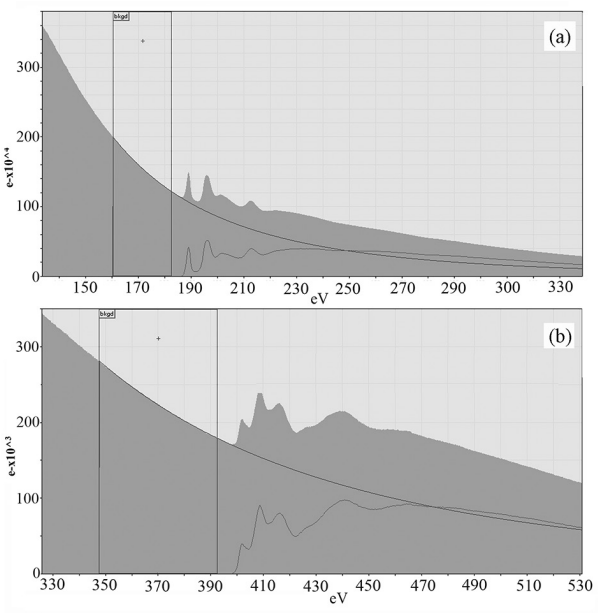

FIGURE 3. EEL-spectra: (**a**) boron *K*-edge with the edge onset at 189 eV and (**b**) nitrogen *K*-edge with the edge onset at 409 eV.

pattern with zone axis $00\bar{1}$ and compared them with the observed angles (Table 2). All of the angles are within the measurement error of <1°. The measurement of the angles between adjacent planes and the agreement between calculated and observed angles confirms the identification of qingsongite as c-BN. By analogy with the synthetic compound, qingsongite has space group $F\bar{4}3m$, $Z = 4$.

Powder X-ray diffraction data (Table 3) are taken from Soma et al. (1974) for the synthetic analog with $a = 3.6157$ (10) Å.

OCCURRENCE AND ASSOCIATED MINERALS

The qingsongite-bearing rock fragment comprises three zones: (1) a core of Fe-Ti alloy about 500 μm across is mantled by (2) an inner zone 10–90 μm thick of native Ti, which in turn is partially mantled by (3) an outer zone of aluminosilicate minerals 30–60 μm thick (Yang et al. 2007; Dobrzhinetskaya et al. 2009). A very narrow zone (<1 μm) of Si-Al alloy (Si 78, Al 20, Ti 2, in at%) borders the native Ti adjacent to the aluminosilicate zone, which consists of ~45 modal% coesite, ~15% kyanite, and ~40% of other phases, largely amorphous aluminosilicate with significant Ti, Mg, and alkalis (Yang et al. 2007). Phases present in much smaller amounts include native Fe; TiO_2 II, a high-pressure polymorph of rutile with the αPbO_2 structure; boron carbide of unknown stoichiometry; amorphous carbon; osbornite (TiN); and qingsongite (see Fig. 1), as well as Ti-Si-O and Ti-Al-Si-O grains that are too tiny to be identified (Yang et al. 2007). Coesite forms prisms several tens of mircometers long, but is polycrystalline, and thus interpreted to be pseudomorphs formed after the inversion of stishovite (Yang et al. 2007). One of the remarkable features of coesite (Fig. 6a) is the presence of twin lamellae, which suggests that coesite had been subjected to local stress. However, the origin of the stress is not known—possibilities include stress during crystal growth and stress resulting from the volume change during transformation of stishovite to coesite. Twin lamellae are also present in kyanite (Fig. 6b).

Qingsongite occurs either as inclusions in coesite that also contains inclusions of osbornite (Fig. 2a), in osbornite enclosed in coesite (see Fig. 4 in Dobrzhinetskaya et al. 2009), or as isolated domains together with osbornite and amorphous carbon enclosed in kyanite.

TABLE 1. Calibrations of the fast Fourier transforms from high-resolution images internal standards

hkl	d_{hkl} observed (Å)	d_{hkl} calculated from literature (Å)	$\|\Delta\|$ (Å)[a]
	Platinum[b]		
111	2.222	2.2653	0.043
200	1.970	1.9618	0.008
	Graphite[c]		
$10\bar{1}1$	1.927	2.0318	0.105
$10\bar{1}2$	1.898	1.7994	0.099
0004	1.691	1.6777	0.013
$11\bar{2}2$	1.157	1.1556	0.001
Average $\|\Delta\|$ (s.d.)		0.045 (0.046)	

[a] $|\Delta|$ is the absolute value of the difference between observed and calculated d_{hkl}.
[b] For $a = 3.9236$ Å (Arblaster 1997).
[c] For $a = 2.4617$ Å, $c = 6.7106$ Å (Howe et al. 2002).

TABLE 2. Measured and calculated angles in qingsongite

Planes (*hkl*)	Angle between planes	
	Observed	Calculated[a]
(200)/(111)	54.80°	54.74°
$(\bar{1}11)/(1\bar{1}1)$	69.70°	70.53°
$(200)/(1\bar{1}\,\bar{1})$	54.80°	54.74°

[a] For $a = 3.61$ Å.

TABLE 3. Powder X-ray diffraction data for synthetic qingsongite from Soma et al. (1974) for $a = 3.6157$ (10) Å

I_{rel}	d_{meas} (Å)	d_{calc} (Å)	*h k l*
100	2.088	2.088	1 1 1
8	1.808	1.808	2 0 0
20	1.277	1.278	2 2 0
10	1.0903	1.0904	3 1 1
3	0.9040	0.9039	4 0 0
8	0.8296	0.8295	3 3 1

CONDITIONS OF FORMATION AND ORIGIN

Our initial finding of coesite-kyanite intergrowths together with Fe-Ti alloy and microdiamond in OsIr alloy, which are inclusions in massive chromite ore from the mantle section of a Tibetan ophiolite, led us to conclude that such mineral associations require minimum pressure of 2.8–4 GPa (Yang et al. 2007). However, microstructures of the coesite prisms indicate that they are pseudomorphic after stishovite, implying a pressure >9 GPa. These findings in what appears to be an unmetamorphosed mantle section of ophiolite were startling. The presence of TiO_2 II confirms the stishovite interpretation because at 1300 °C, stability of TiO_2 II requires a pressure within the stishovite field (Withers et al. 2003). The simplest scenario to explain these mineral assemblages is that at least some parts of the rootless podiform chromitites within the Luobusa ophiolite have a deeper origin than was then understood. Further support of a deep upper mantle origin is provided by the presence of exsolution lamellae of coesite and clinopyroxene in chromite, which indicate that the chromite may have had a Ca-Fe_2O_4-(Ca-ferrite)-structure (Yamamoto et al. 2009), a phase that is stable at pressures over 12.5 GPa (Chen et al. 2003; Green 2004). A deep upper mantle origin also has the advantage of explaining

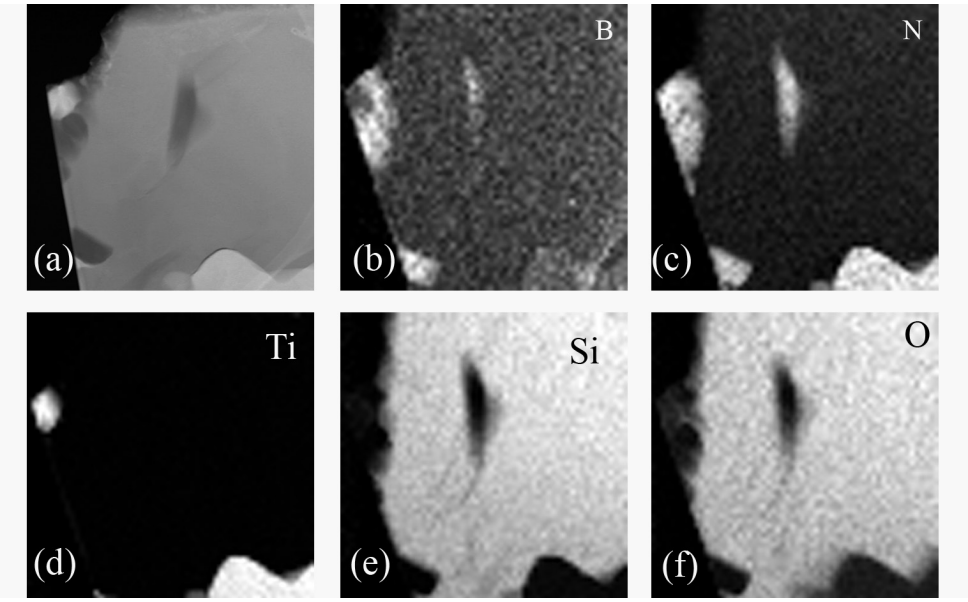

Figure 4. EDX element maps of the area boxed on Figure 2. (**a**) An image of the mapped area, (**b**) boron, (**c**) nitrogen, (**d**) titanium, (**e**) silicon, and (**f**) oxygen.

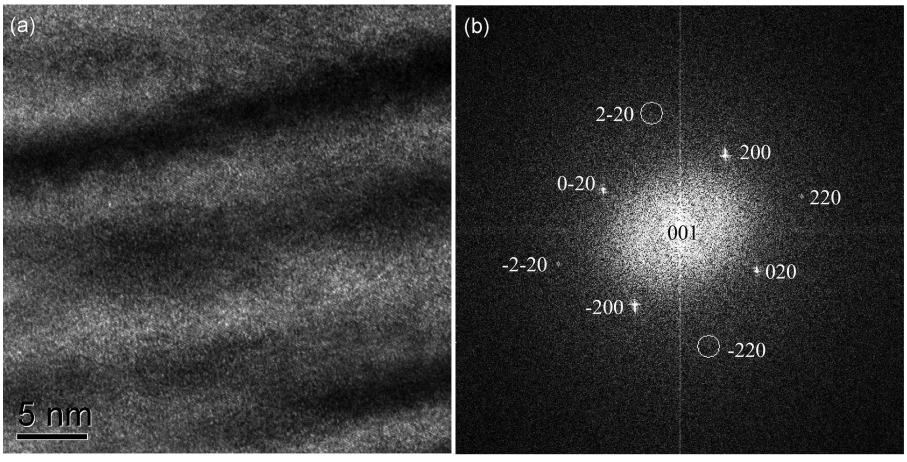

Figure 5. A high-resolution lattice fringe image of BN (**a**) with the corresponding diffraction pattern (FFT) (**b**). The 220 reflections are weak (the positions of $2\bar{2}0$ and $\bar{2}20$ are circled) because the [100] zone axis is not perfectly aligned parallel to the electron beam.

the presence of stishovite as a relic of deeply subducted sediment (e.g., Irifune et al. 1994; Dobrzhinetskaya and Green 2007).

Yang et al. (2007) hypothesized that an impact origin is also a possible alternative explanation for the ultrahigh-pressure phases. However, microstructures in the fragment are inconsistent with shock metamorphism of a crustal rock, i.e., microstructures of the coesite pseudomorphs of stishovite are unlike those reported for either stishovite or coesite in shock-metamorphosed quartz-bearing rocks in impact structures, such as Ries Crater, Germany (Stähle et al. 2008) and Vredefort Dome, South Africa (Martini 1991). A feature common to the shock metamorphosed rocks is the absence for direct conversion of stishovite to coesite, although coesite is later than stishovite. In addition, the N and C isotopic compositions of osbornite have a mantle signature (see below), which is not consistent with the entire fragment being crustal rock that had been subjected to shock metamorphism.

Our temperature estimate of ~1300 °C for the qingsongite-bearing fragment is based on our previous suggestion that after exhumation the fragment remained at a shallow level of the oceanic lithosphere (Dobrzhinetskaya et al. 2009). We are unable to re-confirm this estimate independently, because there are no diagnostic mineral assemblages that could be used as geothermometers in the studied sample. Instead, we consider the constraints imposed by available phase diagrams for the minerals in the fragment and consistent with this temperature and with the probable presence of a chromite polymorph having a Ca-ferrite structure in the chromitite hosting the fragment (Yamamoto et al. 2009). At T ~1300 °C, TiO_2 II and stishovite constrain the pressure to be at

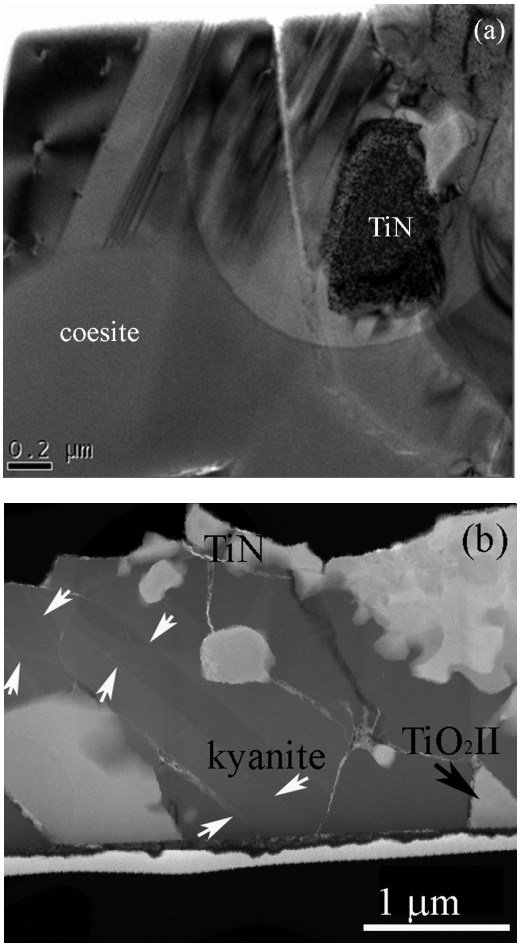

Figure 6. TEM images showing: (**a**) bright-field image of coesite with twin lamellae containing an inclusion of osbornite; (**b**) HAADF image with twin lamellae in kyanite (white arrows) containing inclusions of osbornite and TiO_2 II.

least ~10 GPa (Akaogi et al. 2011; Withers et al. 2003); similarly, the presence of kyanite instead of stishovite + corundum gives a maximum pressure of 14–15 GPa (Schmidt et al. 1997; Liu et al. 2006, cf. Irifune et al. 1995; Ono 1999). Dobrzhinetskaya et al. (2009) suggested that by analogy with coesite, kyanite could have formed from breakdown of stishovite + corundum, in which case the presence of kyanite would not place an upper limit on pressure.

Qingsongite itself provides no new constraints to supplement those indicated by the other phases in the fragment. There are four polymorphs of BN: hexagonal = h-BN, rhombohedral r-BN, wurtzite = w-BN, and cubic (sphalerite/zincblende) = c-BN. Both h-BN and r-BN have layer structures (sp2 bonding) and lower densities compared to w-BN and c-BN, which are characterized by sp3 bonding. Cubic-BN has been synthesized over a wide range of *P-T* conditions, namely from <2 to 60 GPa at temperatures ranging from 400 °C to about 3000 °C (e.g., Bundy and Wentorf 1963; Corrigan and Bundy 1975; Singh et al. 1995a, 1995b; Setaka and Sato 1992; Demazeau et al. 1995; Will et al. 2000). Solozhenko (1995) calculated from the extensive experimental studies on the c-BN ↔ h-BN transition (Fig. 7) that it occurred at a significantly lower pressure than had been determined by Bundy and Wentorf (1963) and cited by Corrigan and Bundy (1975). Kern et al. (1999) performed ab initio calculations of the transition that provided support for Solozhenko's (1995) "equilibrium diagram," but noted that small variations of the free energy can result in large shifts in the transition temperature. Will et al. (2000) performed experiments showing that c-BN is stable at relatively low pressures and that kinetics play a decisive role in the transformation h-BN ↔ c-BN. Wang et al. (2004) and Wang and Yang (2005) suggested that synthesis of c-BN at pressures lower than indicated by Corrigan and Bundy (1975) could be attributed to surface tension of nanosized grains, the so-called nanosize-induced interior pressure on the Gibbs free energy of critical nuclei. Hu et al. (2011) calculated a phase diagram in which the triple point of c-BN, h-BN, and liquid is shifted from the position shown in Figure 7 to about 2700 K and 1.5 GPa as crystal size decreases to 2 nm. In summary, whatever the interpretation of the stability range of c-BN, all of them fall within the range constrained by the other phases in the fragment of our studies.

Mössbauer spectroscopy of massive chromite ores, which the highly reduced qingsongite-bearing fragment was recovered from, gave $Fe^{3+}/\Sigma Fe = 0.42$ (Ruskov et al. 2010). Ruskov et al. (2010) explained the surprisingly high proportion of Fe^{3+} in the "reduced" massive ores by stabilization of Fe^{3+} in a high-pressure polymorph of chromite deep in the upper mantle through a mechanism such as charge-coupled substitution or creation of oxygen vacancies, accompanied by Fe disproportionation to balance charge.

Nitrogen and carbon isotopes provide important constraints on the origin of qingsongite. Citing compositions of $\delta^{15}N = -10.4 \pm 3‰$ and $\delta^{13}C = +5 \pm 7‰$ in osbornite led Dobrzhinetskaya et al. (2009) to conclude that the N clearly had a mantle origin, and C could not be derived from organic material (Fig. 8). The high uncertainty in $\delta^{13}C$ is due to small amount of C in osbornite. This $\delta^{15}N$ is more negative than the composition generally accepted for the upper mantle (~ –5‰, e.g., Cartigny and Ader 2003) and with the N found in basaltic vesicles, but N in some peridotitic diamonds have $\delta^{15}N = -10‰$ or less (Fuxian diamonds, see Javoy 1997; Cartigny et al. 1997). Most iron meteorites have a more negative signature ($\delta^{15}N = -50$ to $-90‰$, Prombo and Clayton 1993). These systematics are consistent with the N in our sample containing a component coming from deep in the mantle, or conceivably even from the core.

The protolith of the coesite-kyanite fragment containing qingsongite and osbornite inclusions probably has a crustal origin, because high contents of SiO_2 and Al_2O_3 are not typical for any known mantle reservoirs. The bulk composition of coesite + kyanite + amorphous material corresponds approximately to a mixture of SiO_2, Al_2SiO_5, $(K,Na)AlSi_3O_8$, and $MgTiO_3$, i.e., to a mixture of illite and other clays or muscovite with quartz, possibly with minor chlorite, assemblages characteristic of unmetamorphosed or low-grade pelitic metasediments. Non-pegmatitic muscovite is reported to contain 6–270 ppm B (Grew 2002) and illite and illite-clay mixtures, about 23–2000 ppm B (Lerman 1965; Reynolds 1965a, 1965b; Couch and Grim 1968), sufficient for the formation of qingsongite if retained during deep subduction. The estimated composition differs from a typical pelite in having relatively high Ti content, absence of Fe and presence of N of mantle origin, i.e., the studied fragment is a hybrid consisting of crustal material "contaminated" by incorporation of mantle components.

Discussion and conclusions

Our proposed scenario (Fig. 9) starts with a pelitic sediment or low-grade metapelitic sediment that was subducted to mid-mantle depths as was previously conceptualized by Robinson et al. (2004). Yamamoto et al. (2009) presented evidence that the chromitite from which the fragment was extracted had also been deeply buried. Yamamoto et al. (2013) reported spot analyses of zircons extracted from Luobusa podiform chromitite giving ages as old as Late Archean, and interpreted the zircons as xenocrysts entrained in chromitites after residing in mantle peridotite, i.e., the zircons represent crustal contamination of upper mantle under the Neo-Tethys Ocean. As regards metamorphism of the fragment during deep subduction, experiments on pelitic sediments, basalt, and andesite, the high-Si variety of muscovite, phengite, would remain stable until deeply buried, and only at 9–11 GPa would break down to K-hollandite, a high-pressure form of $(K,Na)AlSi_3O_8$ (e.g., Schmidt 1996; Domanik and Holloway 1996, 2000). Yang et al. (2007) cited a microstructural similarity between the coesite psudomorphs in the fragment and stishovite prisms crystallizing with K-hollandite from a 50% SiO_2 and 50% $KAlSi_3O_8$ mixture at T = 900 °C, P = 10 GPa, in an experimental run by Dobrzhinetskaya and Green (2007). At this juncture, interaction with the highly reducing environment and Fe-Ti metal in the mantle could have resulted in the anomalous compositional features of the fragment. For example, oxygen fugacity could be so low that Fe^{2+} in silicate minerals or melt is no longer stable and iron separates out as Fe metal, leaving the fragment depleted in Fe. Under the highly reducing conditions, mantle N combined with Ti and B to form osbornite and qingsongite, respectively. The age of osbornite and qingsongite formation is not tightly constrained. These minerals could have formed over 500 Ma ago when crustal materials were subducted into the mantle, according to the scenario for tectonic evolution suggested by Yamamoto et al. (2013). However, a more plausible estimate is given by the depleted Os-model age of 234 ± 3 Ma for a component of the podiform chromitites (Shi et al. 2007; Yamamoto et al. 2009). This component together with ultrahigh-pressure minerals were transported upward by mantle upwelling most likely prior to the first stage of formation of the ophiolite and podiform chromitite at ca. 170 Ma, but certainly before ca. 120 Ma, the age of supra-subduction magmatism dated by zircon (Robinson et al. 2004; Yamamoto et al. 2009, 2013); i.e., the range 120–170 Ma is the minimum possible age for osbornite and qingsongite in the Luobusa chromitite.

The inversion of stishovite to coesite involves a substantial volume increase (over 40% from volumes measured at room temperature and 1 bar pressure). However, except for the lamellar twinning in coesite and kyanite (Figs. 6a and 6b), and possible dislocations in coesite (see left upper corner of image on Fig. 6a), no other microstructures related to deformation or volume change were observed during our studies of the nitrides-coesite-kyanite-bearing fragment. Possibly, the neighboring amorphous phase accommodated the strain through plastic deformation or Si diffused out of the fragment into the neighboring Fe-Ti alloy, a possibility suggested by the narrow zone (<1 μm) of Si-Al alloy between the aluminosilicate fragment and native Ti bordering the Fe-Ti alloy (Fig. 1). As noted by Dobrzhinetskaya et al. (2009), coesite did not invert to quartz during later stages of exhumation as most likely water fugacity was too low.

In summary, qingsongite has a mixed parentage—B most likely crustal, but N most likely mantle, nonetheless, qingsongite is a mantle mineral, because it is composed of mantle N combined with B under highly reducing conditions. Such a combination is not a surprise for a crustal material that once, at least, was deeply subducted and then exhumed back to the shallow levels of Earth. For example, Sumino et al. (2011) showed that in the Kokchetav massif, Kazakhstan, microdiamonds crystallized from crustal carbon and enclosed in crustal ultrahigh pressure metamorphic rocks subducted to a depth of ~210 km, contain inclusion-hosted $^3He/^4He$ of (3.3–6.5) × 10^{-5}. This range of $^3He/^4He$ ratio is close

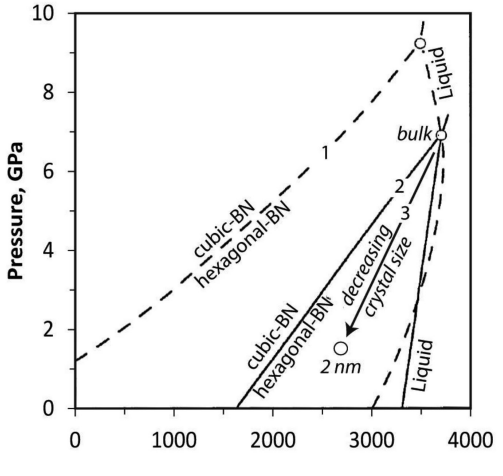

Figure 7. Boron nitride phase diagram modified from Solozhenko (1995). The c-BN–h-BN–liquid triple point is marked by a circle. (1) Dashed line based on Bundy and Wentworth (1963) is essentially the same as reported by Corrigan and Bundy (1975). (2) Solid line is based on the "equilibrium diagram" derived by Solozhenko et al. (1990). (3) Arrow labeled in italics indicates decrease in pressure and temperature of the triple point with decrease in crystal size to 2 nm calculated from the thermodynamic theory at the nanoscale by Hu et al. (2011).

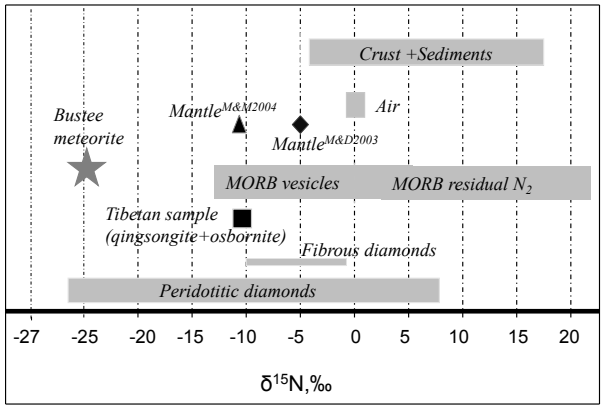

Figure 8. Nitrogen isotope characteristics of selected materials. Data source: Bustee meteorite (Carr and Pillinger 1984); Tibetan sample (this study); Crust, Sediments, Air, MORB, and diamonds (Javoy 1997); Mantle$^{M\&D2003}$ (Marty and Duphas 2003) and Mantle$^{M\&M2004}$ (Mohaparta and Murty 2004).

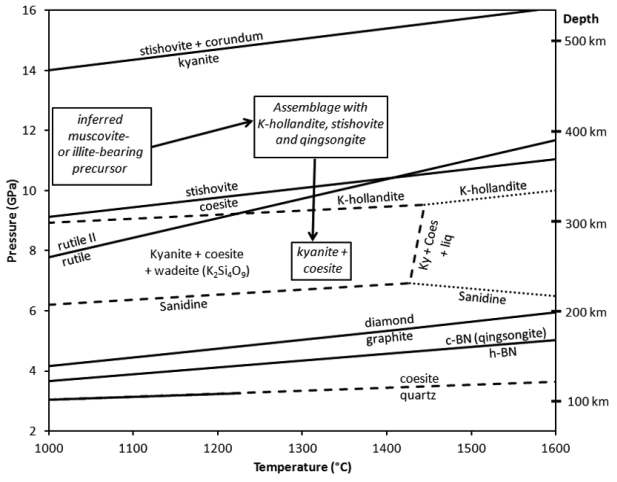

FIGURE 9. Pressure-temperature diagram showing reactions relevant to the formation conditions and origin of qingsongite. Sources of data: hexagonal-BN (h-BN) ↔ c-BN (Corrigan and Bundy 1975); graphite ↔ diamond (Day 2012); reactions involving K-bearing phases in the system $KAlSi_3O_8$, dashed where some experimental constraints and dotted where estimated (simplified from Urakawa et al. 1994); coesite ↔ stishovite (Akaogi et al. 2011); rutile ↔ rutile II (Withers et al. 2003); kyanite ↔ stishovite + corundum (Schmidt et al. 1997); coesite ↔ quartz, dashed where extrapolated (Hemingway et al. 1998). Boxes and arrows mark the evolution of the qingsongite-bearing fragment.

to that of noble gases enriched in a primordial component and delivered from the deep mantle by plumes to oceanic island environments, i.e., the Kokchetav diamond-bearing rocks were "hybridized" with the mantle components. By analogy, we suggest that the qingsongite-bearing fragment has both crustal and mantle geochemical characteristics.

IMPLICATIONS

Our discovery of qingsongite in the Luobusa ophiolite, together with the discoveries of osbornite, coesite pseudomorphs of stishovite discovered by Yang et al. (2007) and Dobrzhinetskaya et al. (2009), coesite exsolution lamellae in chromite (Yamamoto et al. 2009), and Archean zircons by Yamamoto et al. (2013), have important implications for our current understanding of the process and depths of formation of podiform chromitites in the mantle sections of ophiolites, since these have now been shown to contain mineral assemblages indicative of deep subduction of crustal material.

The presence of qingsongite also has implications for understanding the recycling of crustal material back to the Earth's mantle, including to depths of several hundred kilometers. Boron is potentially an ideal tracer of material from Earth's surface, because boron is concentrated there by at least two orders of magnitude compared to primitive mantle. Qingsongite is the first reported mineral of mantle origin containing essential boron, but it is not the only evidence of boron concentrations in a mantle mineral; blue diamonds of type IIb containing up to ~8 ppm B (Gaillou et al. 2012) is another. Qingsongite and crustal zircons reported by Yamamoto et al. (2013) are among the crustal material in the Luobusa ophiolite that is forcing us to realize just how deep Earth's upper continental crust can be subducted—and stranded over long periods of time—in Earth's mantle. Search for other new boron-bearing minerals in the mantle environments should be continued.

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