Boron in natural type IIb blue diamonds: Chemical and spectroscopic measurements

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ABSTRACT

The presence of boron in the structure of diamond is rare in nature, and even when present, reported values are ≤0.5 ppm. This study used various spectroscopic methods and time-of-flight (ToF-) SIMS to characterize and analyze for boron in natural type IIb blue diamonds, including the well-known Hope and the Blue Heart diamonds, and on one high-pressure, high-temperature annealed natural stone. Infrared spectroscopy measurements reveal uncompensated boron values as large as 1.72 ± 0.15 ppm, which is significantly higher than the previously reported maximum of 0.5 ppm. ToF-SIMS analyses gave spot total boron concentrations as high as 8.4 ± 1.1 ppm for the Hope diamond to less than 0.08 ppm in other blue diamonds. By comparison, a type Ia diamond did not show detectable boron. ToF-SIMS analyses revealed strong zoning of boron in some diamonds, which was confirmed by mapping the uncompensated boron using synchrotron infrared spectroscopy. This greater range of boron concentrations compared to previous studies might be explained by the larger number of natural diamonds analyzed here, 78, compared to <10 samples reported in the literature. The samples in this study are all gem-quality diamonds, including some Intense to Fancy-Deep blue diamonds; color intensity, however, only loosely correlates with the boron content. Boron is also likely responsible for the phosphorescence emissions of type IIb diamonds, in the red at 660 nm and in the blue-green at 500 nm. Our results are consistent with previous work suggesting that the emissions are caused by donor-acceptor pair recombination processes involving boron and other defects. The exact nature of the phosphorescence processes is still not fully understood, but likely involves complex steps of charge carrier trapping and detrapping.

Keywords: Type IIb diamonds, boron, ToF-SIMS, synchrotron FTIR, cathodoluminescence, phosphorescence, plastic deformation

INTRODUCTION

Diamonds are messengers from the inner Earth. Their hardness and chemical inertness preserve trapped mineral inclusions during their ascent to the surface that are some of the deepest, most pristine, and oldest samples of the Earth’s mantle and provide excellent clues to the geodynamics of the deep and early Earth (e.g., Richardson et al. 1984, 1993; Pearson et al. 1998; Cartigny 2005; Stachel et al. 2005; Stachel and Harris 2009; Gurney et al. 2010). Although the included minerals have been extensively studied, the diamonds themselves and the processes by which they formed are less well understood (e.g., Collins 1999; Cartigny 2005; Stachel et al. 2005). Studying defects and impurities in the diamond structure also might provide insights into the forces and conditions by which the diamonds formed. For example, one such impurity that is particularly intriguing is boron (B). Why is it found in only a tiny fraction of natural diamonds (less than 0.1% in the most productive deposit of B-containing diamonds, the Premier Mine in South Africa; King et al. 1998), and only in those with no (or low) nitrogen (N)? How is it incorporated into the diamonds, and what is its source, e.g., crustal material from subducting tectonic plates or pure mantle material? The rarity and unusual compositions of B-containing diamonds suggest that they might provide unique insights into processes at work in the Earth’s mantle. Investigations into the role of B in natural diamonds, however, face some daunting challenges. The low concentration of B in natural diamonds (typically <1 ppm) has inhibited meaningful B isotopic measurements, and even the determination of B concentrations in natural diamonds is difficult and rarely has been performed (Collins and Williams 1971; Lightowlers and Collins 1976; Von Windheim et al. 1993; Wynands et al. 1994; Fisher et al. 2009). The analyses that are reported typically are bulk values (obtained by destructive means) and provide no information about the distribution of the B in the diamonds. A first step in deciphering the story behind these diamonds is to better understand the characteristics of B in the diamonds. In the current study, we use various spectroscopic and analytical methods, including time-of-flight secondary ion mass spectrometry (ToF-SIMS), to measure concentrations, and investigate the distribution and properties of B in natural diamonds, including the Smithsonian Institution’s renowned 45.52 carat Hope and 30.62 carat Blue Heart diamonds.

Boron is known to give a blue color to diamond (e.g., Collins 1982), and this hue is one of the rarest and most valuable on the diamond market today. At a Sotheby’s auction in 2009, the price per carat reached $1.3 M for a 7.03 ct blue stone. Most