Graphite paradox in Baikal geyserite paleovalley, Russia

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ABSTRACT

Natural graphite, a polygenic mineral, is a product of regional, contact, impact metamorphism, and magmatic or fluid deposition. In fluid-deposited graphite, aqueous C-O-H systems play a special role in determining the characteristics of hydrothermal products by shifting the chemical equilibrium. From this viewpoint, the recently discovered carboniferous mineralization in the Baikal hydrothermalites has attracted increasing interest with regard to graphite crystallization under the influence of low-pressure low-temperature (LPLT) carboniferous H2O-rich fluids. Herein, we studied graphite mineralization in the geyserites and travertines of the Baikal geyserite paleovalley (Eastern Siberia, Russia) by applying a multitude of mineralogical studies. Optical, scanning, transmission electron, and atomic force microscopy, energy-dispersive spectroscopy, Raman spectroscopy, and carbon isotopic composition analyses of graphite, carbonate carbon, and oxygen in both the hydrothermalites and host rocks were conducted. The obtained results revealed several peculiar features regarding the graphite in geyserites and travertines. We found that Baikal graphite, earlier predicted to be a product of hydrothermalites, generally occurs as a relict graphite of the host metamorphic rocks with partial in situ redeposition. The newly formed LPLT fluid-deposited graphite is characterized by micrometer- and submicrometer-sized idiomorphic crystallites overgrown on the relict metamorphic graphite seeds and between calcite sinter zones during the last stage of travertine formation. The results present additional valuable data for understanding the mechanism, range of the formation conditions, and typomorphism of fluid-deposited graphite with probable crystallization from carbon solution in the C-O-H system at LPLT conditions.

Keywords: Graphite, geyserite, travertine, hydrothermal conditions, C-O-H fluid, fluid deposition, paleovalley, Baikal rift zone

INTRODUCTION

Natural graphite is formed either from organic matter during metamorphic processes (regional, contact, and impact metamorphism) or from fluid mineralization resulting from carbon-containing fluids (Beyssac et al. 2002, 2003; Luque et al. 2012; Jaszczak et al. 2003, 2007; Pasteris and Wopenka 1991; Shumilova 2003; Shumilova et al. 2018; Wopenka and Pasteris 1993, and others). Metamorphic graphite is characterized by a wide range of crystallinity levels (from poorly crystalline to high ordered crystalline structures) resulting from a multitude of metamorphic grades, and can be used for thermodynamic calculations (Beyssac et al. 2002, 2003; Wopenka and Pasteris 1993). Fluid-deposited graphite, regardless of its formation conditions, differs from the metamorphic graphite by a universal high crystalline structure and has different well-shaped crystalline habits (Luque et al. 1998, 2009; Luque and Rodas 1999; Jaszczak et al. 2003, 2007; Pasteris 1999), in contrast to the preferable colloform, cryptocrystalline, and flaky graphite crystals found in metamorphic rocks. Some studies have stated that metamorphic and fluid-deposited varieties can occur simultaneously in the same geological object, and sometimes, fluid-deposited graphite can overgrow the earlier formed metamorphic graphite (Luque et al. 2012). The nature of a certain graphite variety can be identified via isotopic studies, which utilize a series of geological data to recognize the different carbon sources of magmatic and sedimentary carbonates, organic matter assimilation, and devolatilization origin and mixture of different graphite carbon sources (Luque et al. 2012). Fluid-deposited graphite is a result of carbon-bearing CO2, CO2+CH4, CO2+CH4+H2O, and CH4 fluids, where H2O plays an important role in both graphite initial deposition and precipitation (Duke and Rumble 1986). Open C-O-H systems with H2O-rich fluid are of increasing interest for understanding fluid-deposited graphite formation. Thus, the graphite occurrences in the Late Quaternary hydrothermalites formed from the aqueous fluid (travertines and geyserites) of the Baikal rift zone (Danilova et al. 2016; Shumilova and Danilova 2009; Shumilova et al. 2011; Sklyarov et al. 2014) are of special interest.

Hydrothermal sources are also the subjects of intensive research and use (Altunel and Hancock 1993; Pentecost and Viles 1994; Pentecost 1995a, 1995b; Minissale et al. 2002; Jones and Renaut 2003; Lund et al. 2005; Omelon et al. 2006; Renaut et al. 2008; Crosse et al. 2009; Gibert et al. 2009; Shumilova et al. 2018, and others). As these sources are widespread, several of