The origin of the green color of variscite

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ABSTRACT

The color of variscite from three different localities (Pannecé, France; Sarrabus, Sardinia; Ervedosa, Portugal) and metavariscite from Utah was investigated by diffuse reflectance and EPR spectroscopy. These samples contain low levels of transition elements such as V, Cr, and Fe, the relative concentration of which varies with origin, although they remain in the wt% range. The presence of peculiar antiresonance features indicates that octahedral Cr$^{3+}$ ions are responsible for the absorption bands that cause the green coloration of variscite and metavariscite. Trivalent iron ions, which give only a weak absorption band in some samples, and V$^{3+}$ ions do not contribute to the green coloration of the samples from these locations. The crystal-field splitting and B Racah parameter of Cr$^{3+}$ in variscite and metavariscite are 1590 and 657 cm$^{-1}$ and 1610 and 575 cm$^{-1}$, respectively. These values indicate a weak crystal field and an important Cr-O covalence. Electron paramagnetic resonance spectra show the presence of minor amounts (300–500 ppm) of vanadyl groups substituted for Al. The absence of V$^{3+}$ indicates that variscite and metavariscite formed in an oxidizing environment.

INTRODUCTION

Variscite and metavariscite, AlPO$_4$⋅2H$_2$O, are relatively rare hydrated aluminum phosphates which form at low temperatures as a result of phosphate-bearing surface solutions reacting with aluminum-rich rocks. They are usually deposited with other secondary phosphate minerals, such as apatite, wavellite, and crandallite, as a cementing material in various rocks, including schists, quartzite, or igneous rocks (Larsen 1942). Although the pure phases are white and transparent, variscite and metavariscite occur as beautiful green minerals with yellow to blue hues, and may be used as an ornamental stone. Because of their green color, they are sometimes confused with turquoise. Variscite has been used as an ornamental stone since the early Neolithic. Worked into beads and pendants as early as 4000 BCE, variscite jewels have been found in several parts of western Europe (Sheridan 2000), as in the Neolithic mines of Can Tintorer, Cataluna, Spain (Villalba 2002), and deposited in tombs throughout the megalithic fringe of Atlantic Europe, as at Carnac, French Brittany (Damour 1864).

The origin of the typical apple-green color of variscite and metavariscite is not clearly understood. Early qualitative studies, based on spectroscopic observations, indicated that the color was due to Cr$^{3+}$ (Anderson 1954, 1955, in Fritsch and Rossman 1987). However, the green color of variscite and metavariscite samples from Arkansas has also been attributed to the presence of small quantities of V$^{4+}$ and Cr$^{3+}$ (Foster and Schaller 1966). As noted by Marty et al. (1999), “the exact mechanism of coloration of variscite is still poorly understood.” The optical absorption spectrum of a variscite sample from Fairfield, Utah, suggested the presence of V$^{3+}$ (Rossman 2004). Such uncertainty arises from the coincidental position of the absorption bands of V$^{3+}$ and Cr$^{3+}$ in several minerals, including garnets, spodumene, beryl, muscovite, etc. (Burns 1993). The variscite structure also accommodates other transition elements, such as ferric iron, and variscite forms a series with strengite, FePO$_4$⋅2H$_2$O. The fine-grained texture, with grain sizes reaching about 10 μm (Larsen 1942), limits our knowledge of the crystal chemistry of minor and trace components in these minerals. In the presence of associated impurity phases, such as ubiquitous Fe-oxides, it is necessary to use spectroscopic methods, which are sensitive only to transition elements located in a diamagnetic matrix. This manuscript presents the first comparative study of the spectroscopic properties of variscite and metavariscite. Diffuse reflectance spectroscopy is a convenient method to investigate crystal-field transitions in polycrystalline samples, as shown for Cr-bearing phyllosilicates (Calas et al. 1984). We have used this method, together with electron paramagnetic resonance (EPR), to show that Cr$^{3+}$ ions are responsible for the coloration of variscite and metavariscite samples from various localities with different concentrations of Cr and V. Similar absorption bands arising from Cr$^{3+}$ ions have recently been obtained from diffuse reflectance spectra of Neolithic variscite jewels from Western Europe (Galoisy et al. in prep.). The absence of V$^{3+}$ and the evidence of minor vanadyl groups indicate that oxidizing conditions prevailed during the formation of these low temperature minerals.

SAMPLE DESCRIPTION

Variscite samples from three different localities and one metavariscite sample were selected on account of their range in Cr and V contents. Variscite samples from the stratabound polymetallic deposit at Sarrabus, Sardinia (Italy) have a pale green color, with no visible inclusions. Optical microscopy was