**LETTER**

**Carbon oxides in cordierite channels: Determination of CO₂ isotopic species and CO by single crystal IR spectroscopy**

**VLADIMIR M. KHOMENKO¹,²,* AND KLAUS LANGER²**

¹Institute of Geochemistry, Mineralogy and Ore Formation, Ukrainian Academy of Science, pr. Palladina 34, 252142 Kyiv, Ukraine
²Institut für Angewandte Geowissenschaften, Technische Universität Berlin, Ernst-Reuter-Platz 1, D-10623 Berlin, Germany

**ABSTRACT**

Polarized IR-absorption spectroscopy in the range 7000–1000 cm⁻¹ has been used to examine natural cordierites of different geological origin and chemical composition. In the literature there is much information on H₂O and CO₂, as channel constituents in cordierite, though no isotopic species of these molecules have been distinguished. We newly identify ¹²C¹⁶O, ¹³C¹⁶O, ¹²C¹⁸O, as well as ¹²C¹³O from the single-crystal polarized IR spectra. The vibrational parameters, the temperature behavior, and polarization dependence of the identified carbon oxide molecules were studied in the temperature range 80–700 K. The molecular axes of the CO₂ and CO species are parallel to the a-axis of cordierite crystals. Repeated spectral measurements after heating confirm the low mobility along the c-axis channels of CO₂ and CO molecules at temperatures below 700 K. On the other hand, vibrational frequencies of CO₂ and CO species obtained in this investigation are close to those of the vapor phases, suggesting that the molecules are loosely bonded in the large cavities of the silicate framework.

**INTRODUCTION**

The most CO₂-rich cordierites in nature contain up to 2.2–2.4 wt% CO₂ (Armbruster et al. 1982; Kurepin et al. 1986; Vry et al. 1990; Raase and Schenk 1994). Since the 1960s, there have been numerous X-ray (Armbruster 1985), infrared (Farrell and Newnham 1967; Goldman et al. 1977; Le Breton 1989; Vry et al. 1990), and Raman (Kolesov and Geiger 2000) spectroscopic investigations of the position, orientation, and mobility of the gaseous constituents of cordierite channels. Several spectroscopic studies, most of them being carried out on powder samples, reported the presence of four to five bands assigned to CO₂, namely at 2283, 2307, 2348, 2352, and 2390 cm⁻¹ (Goldman et al. 1977; Le Breton 1989; Visser et al. 1994). According to unpublished results mentioned by Schreyer (1985), spectra of Mg-cordierites experimentally treated with CO show occasionally only a weak band at 2143 cm⁻¹ indicative of CO. Despite many efforts, some spectroscopic results are still in part controversial, and even older papers (Armbruster 1985; Schreyer 1985; Visser et al. 1994; Kolesov and Geiger 2000) have raised questions concerning varieties and orientation of trapped molecules that are unanswered. The omnipresent band near 1950 cm⁻¹ (in all three polarizations) in cordierite spectra can be related to an overtone absorption of a lattice mode, possibly originating in the hexagonal silicate ring (Wood and Nassau 1968; Aines and Rossman 1984).

So far, the literature provides IR-spectroscopic evidence neither for the presence of CO nor for the isotopic species of CO₂. However, it is well known that the ¹³C/¹²C ratio of about 90:1 is roughly, but not exactly, constant in all natural materials (see Berney and Eggers 1964). The carbon isotope composition ⁸¹⁹⁷⁷C of CO₂ in cordierite from Lapland was determined as −7% by Armbruster et al. (1982). At present, it is not known whether the ⁸¹³C value of carbon dioxide molecules captured in cordierite structural channels mainly reflects the ⁸¹³C of original fluids or is caused by fractionation during cordierite crystallization at different geological events.

According to numerous studies, the linear CO₂ molecule is dominantly located in the large central cavities of the cordierite structural channels (site 0,0,1/4) with the long axis oriented parallel to the a-axis of cordierite (Armbruster and Bloss 1982; Armbruster and Bürgi 1982; Aines and Rossman 1984). This orientation is energetically favorable because the cavity size is longer in the a-axis direction compared to the b-axis direction (Hochella et al. 1979), and fits closely the length of the CO₂ molecule. Some authors mentioned that minor fractions of CO₂ may be oriented parallel to the c- (Armbruster 1985) or b-axis (Kolesov and Geiger 2000).

In the present study we identify isotopic species of CO₂ and CO in cordierite channels by means of polarized single-crystal IR spectroscopy at different temperatures.

**SAMPLES STUDIED AND EXPERIMENTAL METHODS**

**Samples and their preparation**

Ten natural cordierite samples from different localities, characterized by different compositions and temperatures of their formation were studied (Table 1). Fragments of these cordierite crystals were separated from the rock samples and oriented parallel to (100), (010), and/or (001) using their conoscopic interference figures. Then they were ground and polished on both sides to a thickness of 0.05–0.5 mm. The thickness was measured by means of mechanical micrometer with an estimated error of ±0.005 mm.

**Single-crystal IR spectroscopy**

The fundamental vibrational modes (symmetric ν₆, two fold degenerated ν₅, and asymmetric ν₄) of molecular CO₂ have been extensively described in the literature...