Crystal structure-crystal chemistry relationships in the zeolites erionite and offretite

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ABSTRACT

This study clarifies the crystal structure variations and relationships in the zeolites erionite and offretite. The crystal structure analyses used Rietveld analysis of X-ray powder diffraction data, obtained both by synchrotron radiation and conventional X-ray sources, and on diffraction patterns obtained by transmission electron microscopy. The framework Al atoms in erionite are preferentially located in the single six-membered ring of tetrahedra (T2 site), whereas the Si-Al distribution is essentially disordered on the tetrahedral framework sites in offretite. In both zeolites, the center of the cancrinite cage is always occupied by K cations in similar amounts in both minerals. The erionite cage in erionite is occupied by Ca and Na atoms distributed on four distinct cation sites. Mg ions can be present up to 0.8 atoms per cell and are located between the Ca1 and Ca3 sites and very close to the Ca2 site on the symmetry axis. In offretite, the Mg site is located on the trigonal axis of the gmelinite cage and the Mg atoms are bonded to a variable number (five or six) of H2O molecules, depending on the site population. The structural data and TEM analysis clearly show that the crystal chemistry of the extraframework cations, Mg in particular, is a major factor controlling whether erionite or offretite crystallizes, the Si-Al distribution in the framework, and the possible stacking intergrowths of the two minerals.

INTRODUCTION

Erionite and offretite are two natural zeolites of the so-called ABC-6 family (Gottardi and Galli 1985) whose members all have a topology of framework tetrahedra based on different stacking of the 4’-6-8 two-dimensional net (Smith and Bennett 1981; Millward et al. 1985). Erionite (ERI) has an average formula Na,K,Ca,[Al10Si26O72]·30H2O and is hexagonal, with space group symmetry P6/mmc and unit-cell parameters a = 13.15, c = 15.05 Å. Offretite [OFF] has a formula KCaMg[Al16Si10O36]·16H2O, is hexagonal with space group symmetry P63/mmc and unit-cell parameters a = 13.30 and c = 7.60 Å. The framework of both zeolites is composed of columns of cancrinite cages (Staples and Gard 1959; Gard and Tait 1972) connected by a double six-membered ring of tetrahedra (hexagonal prism). The cancrinite cages (or ε-cages) are all similarly oriented in offretite whereas they are alternatively rotated by 60° in erionite. Adjacent columns are linked by single six-membered rings connecting cancrinite cages at the same level, forming the larger cages distinctive of each topology: offretite has gmelinite cages (or 14-hedrons) and wide channels parallel to the c axis delimited by 12-membered rings; erionite has large cages (erionite cages, or 23-hedrons) with the larger openings formed by eight-membered rings. In terms of six-membered rings stacking sequence along c, erionite, and offretite have an AABAAC- and an AAB-periodicity, respectively. The lack of six-membered rings in the C sequence position is the reason for the larger pores in the offretite structure.

Previous structural refinements of erionite indicate that the cancrinite cages are occupied primarily by K, and the erionite cages are occupied by Na, Ca, and Mg distributed on several cation positions located on the symmetry axis and by H2O molecules (Kawahara and Curien 1969; Gard and Tait 1973). Cation sites may also be present near the eight-membered ring shared by two erionite cages, and these sites have been interpreted as being occupied by Na and Ca atoms (Gard and Tait 1973), though a peculiar internal exchange process between the latter cation position and the K site within the cancrinite cage has been observed in dehydrated erionite (Schlenker et al. 1977).

In offretite, the cancrinite cages are also occupied primarily by K, the gmelinite cages are occupied by Mg and H2O molecules, and the axial positions in the large channels delimited by 12-membered rings have several sites for Na and Ca (Bennett and Gard 1967; Gard and Tait 1972). The cation position near the eight-membered rings connecting the gmelinite cage to the main structural channel seems to be largely unoccupied, though partial occupancy by K has been observed in a dehydrated offretite, as the result of internal cation exchange (Mortier et al. 1976a). The presence of a small amount of Ca has been observed inside the hexagonal prisms (or double...