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Structure comparison of co-crystallized 6- and 12-sided large cancrinite crystals

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ABSTRACT

Single crystals of hexagonal and dihexagonal morphology cancrinites, crystallized in the same batch reaction with sodalite, have been characterized by X-ray diffraction analysis. Although the unit cell values are almost identical, Si–O bond lengths are greater for the di-hexagonal form (1.650 Å vs. 1.624 Å) and the Al–O bond lengths are shorter (1.710 Å vs. 1.724 Å), possibly indicating greater T-site Si–Al disorder in the di-hexagonal form. ^{27}Al–MASNMR also indicates that the hexagonal form contains minor occluded $Al(OH)_4^-$ ions (as does the co-crystallized sodalite). In addition to forming homogeneous single crystals, the di-hexagonal form frequently occurs as an overgrowth on hexagonal crystals, indicating that it results from a secondary crystallization, possibly coincident with the dissolution of sodalite coincident with the final phase of fractional crystallization.

1. Introduction

In general in zeolite syntheses crystal morphology is a reliable indicator for crystal structure. In the synthesis of interest here two distinct crystal morphologies turn out to have near identical structures of cancrinite (**CAN**). The samples used in this study were made in a program at GEC (UK) in the early 1960's targeting high density computer coding materials. Sodalite (**SOD**), with a cubic unit cell approximately 9 Å on edge, may be viewed as having a pixel volume of ~one cubic nanometer. Trapping photosensitive molecules in a crystal of **SOD** offered the possibility of a high density information storage material. The program sought to synthesize high quality large crystals of **SOD** – the large **CAN** crystals of the present study were an unwanted by-product. Although the original program was not successful, similar photochromic [1] and cathodochromic [2,3] **SOD** materials were developed by several companies, including military radar phosphors commercialized by the RCA Corp [4]. Our interests in **CAN** focus on catalysts or, in the case of these large crystals, as a host for nano-wire syntheses.

The **CAN** general mineral composition may be expressed as $(Na,K,Ca)_{6+x}(Al_6Si_6O_{24})$ $(CO_3, SO_4, OH, etc.)$, with $x < 2$, with excess salt located in the 12-ring channel. Synthetic products are usually in the sodium form. Its mineral chemistry and crystallography have been reviewed elsewhere [5–7]. It is a zeolitic mineral built from AB stacked puckered sheets of 4-ring connected 6-rings [8,9]. Although generally categorized as a feldspathoid mineral, it is also a member of the large group of so-called ABC-6-ring family of zeolites. Its main structural feature is a 6 Å diameter 12-ring channel formed by six linked columns of stacked 11-hedra "cancrinite cages" ($4^6 6^2 6^3$) (canc) cages in the nomenclature of Smith [10]). Synthetically **CAN** co-crystallizes with **SOD** up to a temperature of about 180 °C in the presence of numerous anions [11] and at higher temperatures in additional association with nepheline [12]. Synthetically it is usually made from sodium aluminosilicate gels with nitrate, carbonate or hydroxide anions. It can also be made with Si/Al ratios > 1 [13], and with Ga replacing Si, Ge replacing Al and in the Ga–Ge form [14,15]. A berylophosphate isotype, tiptopite, is also known [16]. **CAN** occurs in nature associated with **SOD** and nepheline in nepheline syenites, and industrially it co-crystallizes with **SOD** in spent Bayer liquors [17]. Most natural and synthetic **CAN** materials have poor sorption properties resulting from channel blocking entrained salts [18] and intergrowths with other members of the ABC-6-ring zeolites [19,20]. Along with single channel zeolites such as mordenite, Linde-L and mazzite it may be of catalytic interest, particularly in the higher silica compositions where channel blockage is rare [21]. The tight 12-ring channel in **CAN** has dimensions close to that of the important catalytic10-ring zeolite ZSM-5. Such single channel zeolites are also of interest as host materials for photo-sensitive dyes [22], nano-tubes [23], nano-wires [24] and filaments [25].

CAN usually crystallizes as distinctive hexagonal rods, but in a synthesis of these unusually large crystals it was seen to co-crystallize with **SOD** in both 6-sided hexagonal and 12-sided dihexagonal morphologies. The latter have been observed for a high

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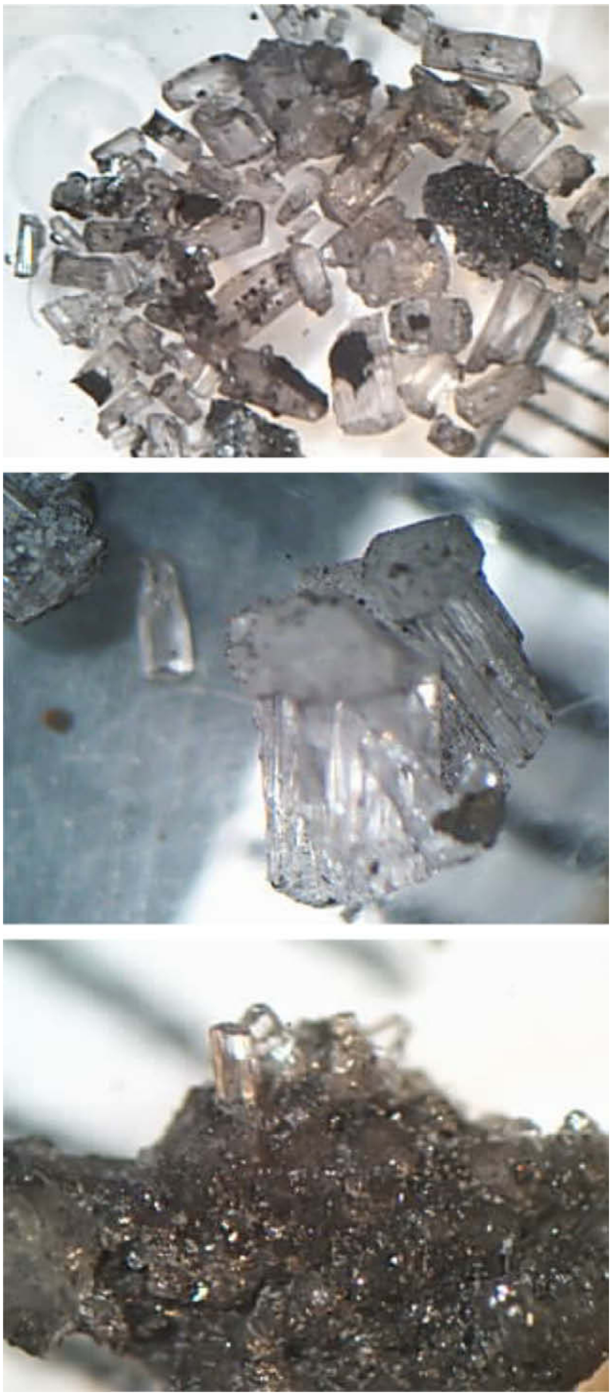

Fig. 1. Top: selection of **CAN** crystals. Middle: **CAN** crystals growing on well faceted SOD crystals. Bottom: di-hexagonal **CAN** crystals on a raft of **SOD** and magnetite (scale = 1 mm divisions).

temperature (300 °C) thiosulfate **CAN** [26], and the morphology is seen in other "cancrinite-like" minerals such as franzite [27] and liottite [28], which introduced the possibility of it being another "cancrinite structural variant", many of which have been described by Merlino [6]. A question was the reason for the morphological duality in a single synthesis; particularly whether or not they are crystallographically identical. Reasons for the duality could be based on changing chemistry during the crystallization, particularly anion concentrations, or whether the hexagonal form was characteristic of (presumed) primary crystallization and the dihexagonal characteristic of a secondary crystallization resulting from the degradation of **SOD**. We and others have observed the replacement of **SOD** by **CAN** at higher temperatures and longer crystallization times but no changes in morphology were reported (or observed in our own work) [11–13,18]. Others have reported the replacement of **CAN** by **SOD** at high temperature and pressure [29]. In the synthesis represented here some **CAN** crystals can be seen to be growing on a base of **SOD** (Fig. 1).

2. Experimental

The sample batch evaluated in this study was donated by E.A.D. White, who made it at high temperature (450 °C) and pressure (1000 atm.) using an unlined Morey type autoclave in a manner described elsewhere [30,31] and a gel composition: $2.85Na_2O:Al_2O_3:2SiO_2:62.5H_2O$ (the experiment was similar to those described in detail in an early work by Barrer and White [32]). The product was a mixed batch of large crystals (up to 3 mm) of **CAN** and **SOD**, many growing off flakes of microcrystalline magnetite corrosion products, indicating that zeolite crystallization occurred mainly on the walls of the autoclave. Nepheline was present in trace amounts and magnetite was ubiquitous, frequently coating and encapsulating the zeolite crystals. **CAN** crystals were up to 3 mm in length and 1 mm in diameter, some showing inclusions and holes parallel to the 'c'-axis. Additionally some crystals were 6-sided (hexagonal, **CAN**-6) and some were 12-sided (dihexagonal, **CAN**-12). Stereo-optical microscope images (x40, x80) of a selection of crystals is shown in Fig. 1, including a cluster of **CAN** crystals growing on well faceted millimeter sized **SOD** crystals, and **CAN** growing on a matrix of small **SOD** crystals and microcrystalline magnetite. A scanning electron micrograph (Hitachi 3500N-VP) of the typical morphology of **CAN**-12 is shown in Fig. 2. It is different from the more regular morphology of a di-hexagonal thiosulfate **CAN** reported by Lindner et al. [26].

For the ^{29}Si–MASNMR and wet chemical analyses (by ICP–AES), crystals of the two **CAN** crystal types and the large **SOD** crystals, reasonably free of adhering magnetite, were separated, cleaned of all visible magnetite by sonicating them several times in distilled water followed by air drying and rolling them with a Teflon coated stirring bar. ^{29}Si–MASNMR measurements were as described by Melchior et al. [33], the mixed **CAN** sample giving a single peak at -87.8 ppm and the **SOD** a single peak at -89.9 ppm. (vs. TMS). Each sample was then was ground to a fine powder

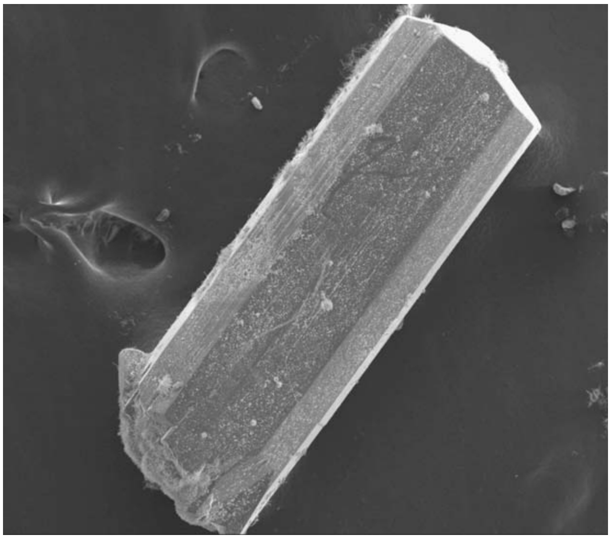

Fig. 2. SEM showing typical morphology of **CAN**-12 (600 μm long).