A New Interpretation of the Structure of Disordered \( \alpha \)-Cristobalite

M. J. Wilson, J. D. Russell, and J. M. Tait

The Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen, AB9 2QJ

Received May 13, 1974

Abstract. Disordered \( \alpha \)-cristobalite which occurs extensively in bentonites, opals and particularly deep-sea cherts, has been previously interpreted in terms of a unidimensionally disordered structure in which cristobalite is interstratified with two-layer tridymite-like sheets. An alternative interpretation is that the structure is essentially tridymitic but that the sheets are stacked with random transverse displacement normal to the \( c \) axis, an arrangement similar to the translational, turbostratic stacking postulated for smectites. This interpretation was arrived at after a comparative study of a silica phase in an Italian bentonite and a deep-sea chert, material which yielded an X-ray powder pattern almost identical with that of disordered \( \alpha \)-cristobalite, but electron diffraction patterns and infrared spectra more consistent with tridymite. It is suggested that this type of silica, which has been described almost universally as cristobalite, is more appropriately referred to as disordered \( \alpha \)-tridymite.

Introduction

Disordered \( \alpha \)-cristobalite has been reported as a minor phase in bentonites (Flörke, 1955) and as a major constituent of certain opals (Jones and Segnit, 1971); more recently it has been found extensively in deep-sea cherts (Rex, 1969; Calvert, 1971a and b). The mineral is usually characterized by a simple X-ray powder pattern consisting of a strong, broad reflection at approximately 4.1 Å and a medium reflection at 2.5 Å. The 4.1 Å reflection is often accompanied by a fairly strong peak or shoulder at 4.3 Å. Flörke (1955) explained this diffraction pattern in terms of a unidimensionally disordered \( \alpha \)-cristobalite structure in which the layers of SiO\(_4\) tetrahedra, although well ordered, are irregularly stacked in the [111] direction normal to the layers. The three-layer cristobalite structure was thought to contain two-layer tridymite-like sequences, variation in this type of disorder resulting in the broadening and shifting of the strong reflections and in the elimination of the weak ones. On this basis the peaks at 4.1 Å and 2.5 Å in the powder pattern correspond to the 101 and 200 reflections, respectively, of \( \alpha \)-cristobalite, whilst the peak at 4.3 Å is attributed to tridymitic domains within the structure. This interpretation seems to have been generally accepted.

The object of the present study is to present an alternative interpretation based on the supposition that the structure is, in fact, dominated by tridymitic two-layer sheets which are stacked with random transverse displacement normal to the \( c \) axis.

Materials and Methods

The two specimens studied in detail were a bentonite and a deep-sea cristobalite chert. The bentonite is from an unknown source in Italy and contains approximately 14 per cent of a
silica phase, which could not be physically separated from the bulk of the montmorillonitic clay. The chert was recovered during the Deep Sea Drilling Project from the Kerguelen Plateau in the Southern Ocean (Eltanin core 47-15) and has been previously extensively studied (Wise et al., 1972; Weaver and Wise, 1972). It is essentially monomineralic and in its morphological and X-ray characteristics is apparently quite typical of deep-sea cristobalite cherts.

The samples were examined by X-ray powder diffraction, electron microscopy and infrared spectroscopy. For X-ray diffraction the samples were mounted in an aluminium holder, powder patterns being recorded by a Philips 2kW diffractometer using iron filtered CoKα radiation. Transmission electron microscope observations and electron-diffraction studies were made using an AEI EM6 instrument, the samples having been ultrasonically dispersed in water and dried down on a carbon-coated copper grid. Infrared spectra (1400-400 cm⁻¹) were recorded on a Grubb-Parsons Spectrometer. Samples were either incorporated in KBr pressed disks (0.3 mg of 1 mg in 170 mg KBr) or sedimented from aqueous suspension and air dried to give self-supporting films (approximately 2 mg/cm²).

Results

Both samples yield X-ray powder patterns similar to that described above, the most characteristic feature being the broad intense reflection at 4.1 Å. The X-ray diffractometer trace of the chert has been previously illustrated by Wise et al. (1972). Under the electron microscope a platy, well-shaped, hexagonal morphology was revealed with individual particles ranging from 0.1 μm to 1 μm in diameter. The flakes in the chert were larger and better formed than those from the bentonite, which were generally clustered together and associated with montmorillonite. A scanning electron microscope study (Weaver and Wise, 1972) has shown that the chert is actually made up of distinctive bladed spherules, individual blades or plates being from 300 to 500 Å thick. Similar spherules have been synthesized by Oehler (1973) who pointed out that the basic platy morphology is characteristic of tridymite and is distinctly different from the octahedral crystal habit of cristobalite

Electron Diffraction. In both samples the platy particles yield a hexagonal diffraction pattern consistent with tridymite. Diffraction from the plates in the bentonite gives a d-spacing of 8.64 Å (Fig. 1A) — measured with respect to the diffraction rings of montmorillonite — corresponding to ahex = 9.98 Å, in general agreement with the a dimension of low tridymite. In fact, the true cell of α-tridymite is orthorhombic although dimensionally it is pseudohexagonal with b₀ = a₀√3. This gives orthorhombic cell parameters of a = 9.98 Å and b = 17.28 Å, in agreement with the values listed by Frondel (1962). A hexagonal lattice giving a d-spacing of 4.32 Å is shown by the plates from the chert (Fig. 1B) but additional weaker reflections again indicate doubling to 8.64 Å. It should be noted that cristobalite with (111) parallel to the electron beam would also give a hexagonal diffraction pattern, but when the patterns are interpreted in this way, the calculated cubic cell edge is 6.11 Å which is irreconcilable with either pseudocubic α-cristobalite (a = 4.97√2 = 7.03 Å) or cubic β-cristobalite (a = 7.13 Å). A prominent feature of both diffraction patterns is the streaking between the reflections along the three principal directions in the (001) plane. This streaking can be accounted for by a stacking disorder although in beidellite it has been interpreted as an expression of deformation within the tetrahedral layers (Gatineau et al., 1972).