Disordered silica with tridymite-like structure in the Twiggs clay

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ABSTRACT

The existence of a disordered silica polymorph dominated by tridymite-like stacking is implied by the long-held interpretation of opaline silica as disordered intergrowths of cristobalite-like and tridymite-like domains. The currently accepted model for diagenetic transformation of amorphous silica also predicts that early formed structures will be dominated by tridymite stacking. Although the cristobalitic end-member (opal-c) and intermediate structures (opal-ct) have long been acknowledged, the tridymitic end-member has not yet been recognized. Evidence for such an end-member is found in 54 Twiggs clay samples examined by X-ray diffraction (XRD). The mineralogy of the samples is dominated by smectite and disordered silica. The silica phase is biogenic in origin and presents an XRD signature consistent with that of line-broadened tridymite, with a broad primary reflection near 4.107 Å (21.6 °2θ), additional broad peaks of lower intensity at approximately 4.328 Å (20.5 °2θ) and 2.50 Å (35.9 °2θ), and lacking diagnostic cristobalite peaks at 3.14 Å (28.5 °2θ) and 2.84 Å (31.5 °2θ). At present, the most widely used classification of disordered silica is a threefold system that recognizes an amorphous phase (opal-a), a cristobalite-like end-member (opal-c), and intermediate structures incorporating both cristobalite and tridymite domains (opal-ct) (Jones and Segnit 1971). This classification does not accommodate a dominantly tridymite-like structure as is observed in the Twiggs clay. The silica phase in these samples is more accurately described as “disordered tridymite.” A new term “opal-t” is proposed to describe this end-member phase.

Keyword: Opal, disordered silica, X-ray diffraction, cristobalite, tridymite, silica diagenesis

INTRODUCTION

Disordered silica is widespread among different rock types, including many sedimentary rocks formed under low-temperature conditions. The source of the silica may be volcanic but is most commonly biogenic (Kastner 1979). Diatoms, radiolaria, and sponges extract silica from typically undersaturated waters, possibly through enzymatic reactions, and produce siliceous skeletons and ornate frustules of amorphous silica (Blatt et al. 1972; Williams and Crerar 1985). Accumulations of biogenic materials undergo varying degrees of diagenetic transformation, and depending on the extent of alteration and impurities present, become diatomites, porcellanites, siliceous shales, and cherts (Murata and Nakata 1974).

The diagenetic transformation of amorphous silica is the subject of many studies, including Murata and Larson (1975), Mizutani (1977), Keller (1984), Williams and Crerar (1985), and Rice et al. (1995). The general diagenetic sequence is transformation from an amorphous phase to progressively more ordered structures. Intermediate disordered structures are believed to consist of both cristobalite and tridymite domains. Increased structural order is achieved through the loss of tridymite stacking, as the structure becomes more cristobalite-like. With continued burial, metastable cristobalite stacking gives way to crypto-crystalline quartz. These transformations are believed to occur through solution-precipitation reactions occurring at relatively low temperatures (50–110 °C) (Murata and Larson 1975; Keller 1984; Williams and Crerar 1985), although evidence for solid-state transformation of amorphous silica to a partially ordered phase was presented by Mizutani (1977).

Most often, X-ray diffraction (XRD) provides the basis for identifying the low-temperature silica polymorphs; however, very small crystallite sizes, disorder within the framework, and the presence of multiple interfering phases present challenges in interpreting the characteristically broad, low-intensity XRD reflections of partially ordered structures. Techniques other than XRD, including transmission electron microscopy (TEM), infrared microscopy (IR), and nuclear magnetic resonance spectroscopy (29Si MAS NMR), have been utilized (Wilson et al. 1974; Jones and Segnit 1975; Sanders 1975; de Jong et al. 1987; Rice et al. 1995), but these efforts have resulted in differing and sometimes conflicting interpretations, and the structure of disordered silica remains imperfectly understood.

The low-temperature polymorphs of silica are most often classified according to the threefold classification scheme developed by Jones and Segnit (1971). This scheme uses crystal structure as revealed by XRD to classify disordered silica into three categories. The first category, opal-a, is a highly disordered...