American Mineralogist, Volume 83, pages 542–545, 1998

HRTEM investigation of microstructures in length-slow chalcedony

HUIFANG XU,[1,*] PETER R. BUSECK,[2] AND GUFENG LUO[3]

[1]Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico 87131-1116, U.S.A.
[2]Department of Geology, Arizona State University, Tempe, Arizona 85287-1404, U.S.A.
[3]Department of Earth Sciences, Nanjing University, Nanjing, Jiangsu 210093, China

ABSTRACT

High-resolution transmission electron microscopy reveals dense Brazil-twin boundaries on the unit-cell scale in length-slow chalcedony. The twins can be considered as the result of stacking of left- and right-handed quartz with a (101) twin composition plane. Although most twin sequences on the unit-cell scale are nonperiodic, moganite-type domains result where they are periodic. It is proposed that the twins formed during rapid crystallization rather than as transformation products of a precursor phase such as moganite. The twin boundaries are energetically less stable than twin-free areas and may indicate non-equilibrium crystallization at a high supersaturation of aqueous SiO_2 species in the parent fluid.

INTRODUCTION

Microcrystalline quartz, which includes length-fast and length-slow chalcedony, chert, and flint, is common in sedimentary and volcanic rocks (Frondel 1978; Flörke et al. 1991). Chalcedony is a variety of fibrous quartz. Length-slow chalcedony is considered to be a precipitate from brine water and therefore an indicator of vanished evaporates (Folk and Pittman 1971; Hattori 1989). Differences between chalcedony and quartz in composition, optical properties, and microstructures at the unit-cell scale were detailed by Flörke et al. (1982, 1991), Midgley (1951), Frondel (1978), Miehe and Graetsch (1992), Heaney and Post (1992), and reviewed by Heaney (1993). X-ray powder diffraction of microcrystalline quartz shows that it contains variable amounts of moganite-type structure, a material that consists of periodic unit-cell twins of left- and right-handed quartz (Miehe and Graetsch 1992; Miehe et al. 1984; Heaney and Post 1992). Selected-area electron diffraction (SAED) and conventional transmission electron microscopy (TEM) studies show that length-fast chalcedony contains moganite domains and dense Brazil twin boundaries (Graetsch et al. 1987; Heaney et al. 1994). Such planar defects also occur in authigenic quartz (Cady et al. 1993). Most planar defects in microcrystalline quartz, including intergrown length-slow and length-fast chalcedony, are apparently caused by Brazil twinning.

There are no reported TEM results of microstructures in length-slow chalcedony, nor any high-resolution TEM results for either length-slow or length-fast chalcedony. In this paper we present high resolution (HR) TEM images of length-slow chalcedony and discuss the twin boundaries in it and other microcrystalline quartz.

SAMPLE AND EXPERIMENTAL METHODS

The sample is from a Tertiary fine-grained conglomerate from Fang Hill, near Lühe, Jiangsu Province, China. A thin section shows zones of length-slow chalcedony separated by narrow, dark, length-fast chalcedony (Fig. 1). The thicknesses of the length-slow zones change along the growth directions of the fibers.

Chalcedony with optically positive elongation was selected for TEM study from a petrographic thin section and mounted on Cu grids. Thin specimens were prepared by Ar-ion bombardment and then coated on one side with a thin carbon layer. SAED and HRTEM images were obtained by using a JEOL-4000EX high-resolution TEM operated at 400 keV. The main obstacle for the TEM investigation was extremely fast irradiation damage under the high-energy electron beam. A charge-coupled device (CCD) camera, which can record images digitally at low electron-beam doses, was used to achieve good defocus

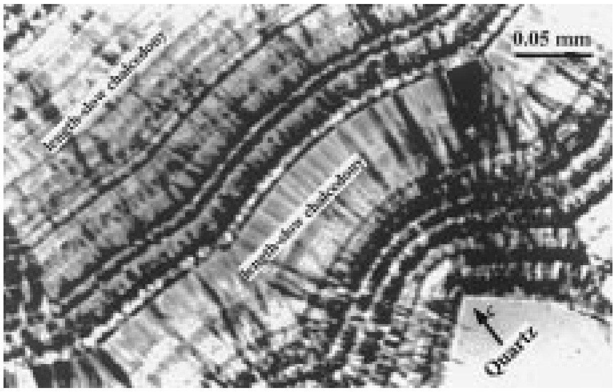

FIGURE 1. Thin section of chalcedony that displays zoning of length-slow and intervening zones of narrow, dark, length-fast chalcedony (cross-polarized light with gypsum plate inserted).

---

* E-mail: hfxu@unm.edu

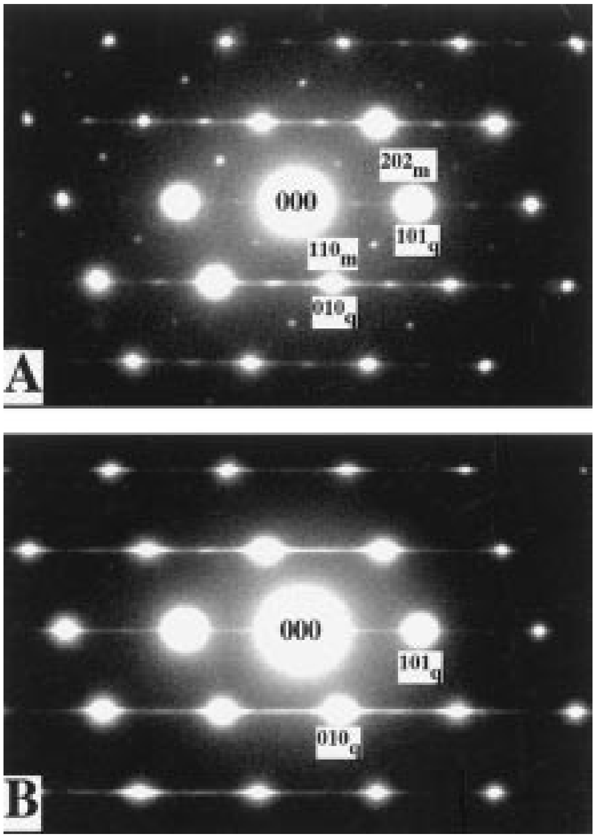

FIGURE 2. $[10\bar{1}]$ SAED patterns of length-slow chalcedony from (**A**) an area with densely periodic and nonperiodic twins and (**B**) an area with only densely nonperiodic twins. The additional weak, sharp reflections in A are caused by intersection of the Ewald sphere with streaked reflections not in the zero-layer reciprocal plane (Heaney 1993).

conditions for the images. Relatively low magnifications and electron beam doses were used to minimize damage.

Simulated HRTEM images were calculated using the MACTEMPAS computer program. The input structure model was based on the structure refinement of Miehe and Graetsch (1992).

RESULTS AND DISCUSSION

SAED patterns from the length-slow chalcedony show strong quartz reflections and streaking along ⟨101⟩* (Fig. 2). SAED patterns from some areas show additional weak reflections that indicate doubling of the unit cell of quartz characterize the moganite-type structure (Fig. 2A) based on XRD and TEM results of Miehe and Graetsch (1992) and Heaney et al. (1994). The streaking is produced by the disordered intergrowth of Brazil twins with composition planes parallel to {101}. HRTEM images from most areas within length-slow bands in our sample show non-periodic arrangements of the {101} composition planes (Fig. 3A). TEM observations from coarser domains show features similar to quartz. Periodic arrangements of one unit layer of left-handed and one unit layer of right-handed quartz, i.e., moganite, occur in areas with densely distributed composition planes (Figs. 3A and 3B). The periodicity of lattice spacing is 6.7 Å perpendicular to {101} (Figs. 3A and 3B). Calculated images show the doubling of the unit cell along (101)* of quartz under certain imaging conditions (Fig. 4). The HRTEM image of periodic twin (moganite) domains showing periodicity doubling (i.e., 6.7 Å periodicity) along (101)* corresponds to the focus condition of −90 nm (Fig. 4). Some areas of length-slow chalcedony fibers contain relatively few composition planes (Fig. 3C). A SAED pattern from the area of Figure 3C containing few twin boundaries shows weak streaking.

Heaney (1993) proposed that chalcedony can precipitate from slightly saturated aqueous solutions at relatively low temperatures (<100 °C) by a spiral growth process, and the solubility of chalcedony is intermediate between the solubilities of opal-A and quartz. Later, Heaney and Davis (1994, 1995) proposed that oscillation of defect

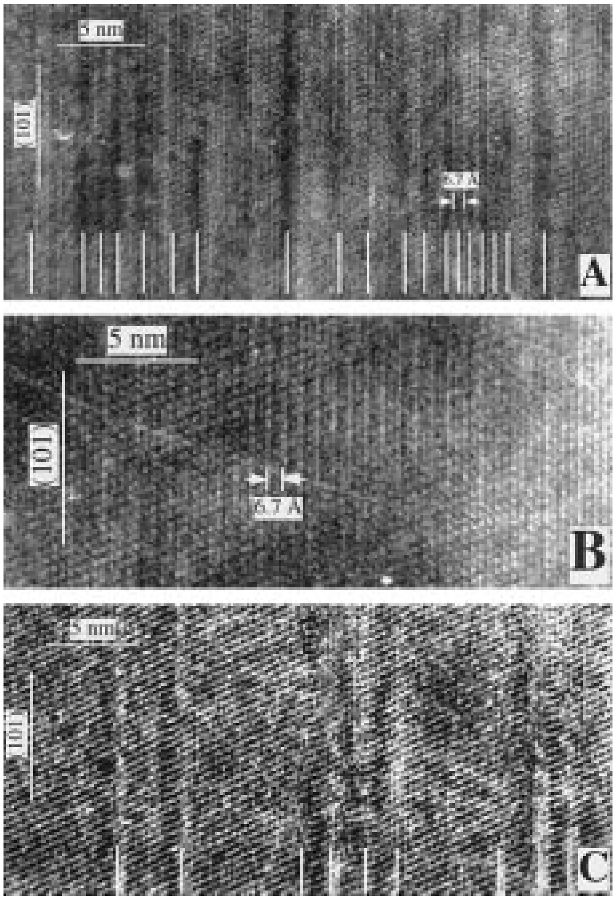

FIGURE 3. HRTEM images of length-slow chalcedony from (**A**) an area with densely nonperiodic twin boundaries and periodic unit-cell twins, (**B**) an area dominated by periodic unit-cell twins with a 6.7 Å periodicity along the normal to {101}, and (**C**) an area with relatively few twin boundaries. Some twin boundaries are marked by white vertical bars. Best viewed at a low angle parallel to the fringes.

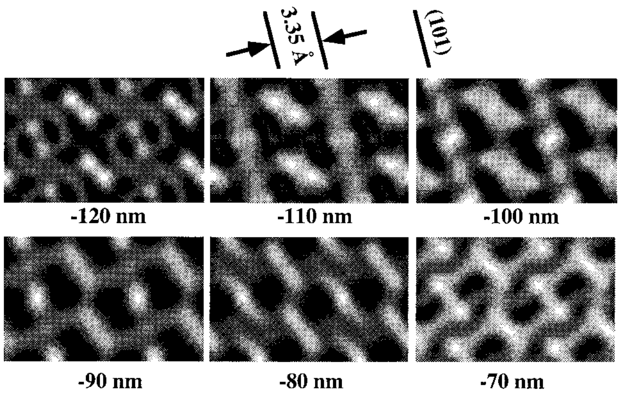

FIGURE 4. Calculated [$\bar{1}$11] zone axis HRTEM image of moganite (see text for detail).

concentrations or zones of quartz and chalcedony result from fluctuating degrees of silica polymerization. In contrast, Wang and Merino (1990), based on their self-organization diffusion model, proposed that chalcedony crystallizes from silica gel.

We think the occurrence of multiple, fine-grained, closely spaced fibers indicates high densities of nuclei during crystallization. Such high densities are related to the nucleation rates, which, in turn, are roughly proportional to the saturation index (Ω) of the fluid (Zhang and Nancollas 1990). A supersaturated solution of aqueous SiO_2 is necessary for producing high concentrations of quartz nuclei for crystallization of chalcedony and other microcrystalline quartz varieties during rapid crystallization.

An interesting phenomenon was observed by Lund (1960), who described two neighboring chambers filled with drusy quartz and chalcedony, respectively, in a fossil coral. The temperature and pressure for the crystallization of silica were presumably the same in both chambers. The only difference is that the chamber with drusy quartz was closed, while the other one was open to the outside environment by a channel. The fluid was presumably slightly over-saturated with respect to quartz in the drusy chamber because of the slow diffusion rate of the fluid into the closed chamber. However, the fluid was probably supersaturated in the chamber with chalcedony because the fluid could pass through the channel and maintain its supersaturated state containing respect to the crystallizing quartz. The drusy quartz is apparently a product of near-equilibrium crystallization from a less supersaturated solution than the solution that resulted in the precipitation of chalcedony. Therefore, the activity of aqueous SiO_2 in the fluid during crystallization was lower in the chamber with drusy quartz than that with chalcedony.

Bonev (1990) suggested that some natural fibrous minerals crystallize under highly non-equilibrium conditions. We infer that the chalcedony and other microcrystalline quartz with dense Brazil twin boundaries and moganite-type domains in this study are also products of non-equilibrium crystallization. The Brazil twins result from growth mistakes during rapid crystallization. These twins take {101} as composition planes because of the relatively low strain energy induced by structural distortion between the neighboring twin lamellae (McLaren and Phakey 1966; McLaren and Pitkethly 1982; Wenk et al. 1988).

Quartz and amorphous silica can result from precipitation of aqueous SiO_2 from supersaturated solutions. The crystallization rate is related to the saturation index by $k(\Omega - 1)^n$ (Rimstidt and Barnes 1980), where k = rate constant and n = adjustable exponent. The activities of aqueous silica in equilibrium with quartz and amorphous silica at different temperatures and pressures are illustrated in Figure 5. If the fluid is in an equilibrium or near-equilibrium state (i.e., Ω is slightly higher than 1), only thermodynamically stable quartz crystallizes. If the fluid is over saturated with respect to amorphous silica (i.e., high Ω), amorphous silica or opal forms. If the solution is under saturated with respect to amorphous silica but supersaturated with respect to quartz, chalcedony with dense Brazil twins forms. A possible region for the crystallization of chalcedony is also labeled in Figure 5.

A fluid that is highly supersaturated with respect to quartz but under saturated with respect to amorphous silica only occurs at relatively low temperature (Fig. 5), which may be the reason for the restricted occurrence of chalcedony to low-temperature rocks. Rapid crystallization of quartz results in growth mistakes of left- and right-handed quartz. Similar phenomena have also been reported for a fibrous cristobalite ("lussatite") with dense stacking faults (Cady and Wenk 1992).

The relatively higher solubilities of chalcedony with

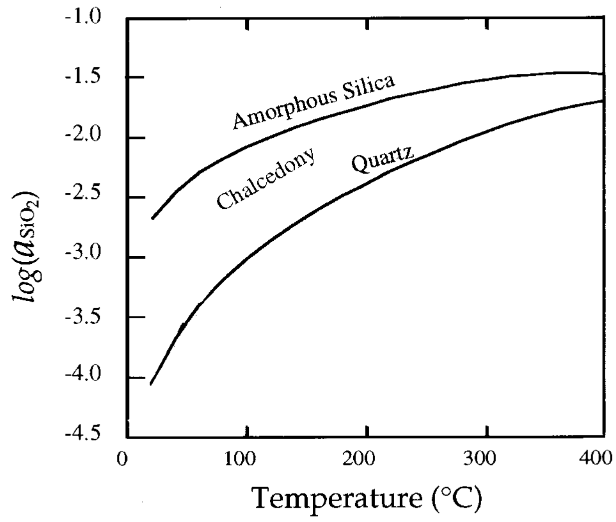

FIGURE 5. Calculated diagram showing the boundaries of aqueous silica activities for quartz and amorphous silica formation as a function of temperature at a pressure of 500 bars. The diagram was calculated using SUPCRT92 software and the database of Johnson et al. (1992). The region for chalcedony formation (between the saturation curves for quartz and amorphous silica) is constrained based on synthesized chalcedony that occurs only below 300 °C.

respect to quartz reported by Fournier (1977) and Walther and Helgeson (1977) indicate that the saturation index of the mother fluids for chalcedony formation is higher than that for quartz. The dense twin boundaries in chalcedony are presumably responsible for the high solubility of chalcedony. We observed that the boundaries amorphize faster than defect-free areas, which indicates the twin boundaries are less stable than twin-free areas. A sudden change in fluid temperature, pressure, or pH could induce supersaturation of aqueous SiO_2. Changes in concentration of NaCl in the fluid can also affect the growth rate of quartz (Huston and Walter 1995). The effect of the dissolved NaCl is similar to supersaturation of the fluid with respect to quartz growth rates. Brines and brine-like fluids in geological systems (Garrels and MacKenzie 1967; Harvie and Weare 1980; Hardie and Eugster 1970) may be a factor contributing to the rapid crystallization of quartz and the formation of chalcedony with dense Brazil twins. Zonation of the twin density in the chalcedony and other microcrystalline quartz may indicate variation of the fluid properties (e.g., activity of aqueous silica) during their crystallization. The observed oscillation between defect-rich and defect-poor zones in the chalcedony may correspond to the oscillation between fast-growth and slow-growth zones proposed by Wang and Merino (1990, 1995).

REFERENCES CITED

Bonev, I.K. (1990) Whisker growth of minerals. Abstracts of the 15th General Meeting of the IMA, Beijing, p. 382–384.

Cady, S.L. and Wenk, H.-R. (1992) An HRTEM investigation of the metastable low-temperature silica phase opal-CT in cherts and porcelanites from the Monterey Formation, CA. Geological Society of America Abstracts with Programs, 24, A-116.

Cady, S.L., Wenk, H.-R., Kilaas, R., and Barber, D.J. (1993) Enantiomorphism and planar defects in length-fast chalcedony. In J.N. Boland and Fitz Gerald, J.D., Eds., Defects and Processes in Solid State: Geoscience Applications, p. 383–400. Elsevier, Amsterdam.

Flörke, O.W., Köhler-Herbertz, B., Langer, K., and Tönges, I. (1982) Water in microcrystalline quartz of volcanic origin: agates. Contribution to Mineralogy and Petrology, 80, 324–333.

Flörke, O.W., Graetsch, H., Martin, B., Röller, K., and Wirth, R. (1991) Nomenclature of micro- and non-crystalline silica minerals, based on structure and microstructure. Neues Jahrbuch für Mineralogie Abhandlungen, 163, 19–42.

Folk, R.L. and Pittman, J.S. (1971) Length-slow chalcedony: a new testament for vanished evaporates. Journal of Sedimentary Petrology, 41, 1045–1058.

Fournier, R.O. (1977) Chemical geothermometers and mixing models for geothermal system. Geothermics, 5, 41–51.

Frondel, C. (1978) Characters of quartz fibers. American Mineralogist, 63, 17–27.

Garrels, R.M. and MacKenzie, F.T. (1967) Origin of the chemical compositions of some springs and lakes. In W. Stumm, Ed., Equilibrium Concepts in Natural Water Systems, p. 222–242. American Chemical Society, Washington, D.C.

Graetsch, H., Flörke, O.W., and Miehe, G. (1987) Structural defects in microcrystalline silica. Physics and Chemistry of Minerals, 14, 249–257.

Hardie, L.A. and Euster, H.P. (1970) The evolution of closed-basin brines. Geological Society of America Special Publication, 3, 273–290.

Harvie, C.E. and Weare, J.H. (1980) The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-Cl-SO_4-H_2O system from zero to high concentration at 25 °C. Geochimica et Cosmochimica Acta, 44, 981–997.

Hattori, I. (1989) Length-slow chalcedony in sedimentary rocks of the Mesozoic allochthonous terrain in central Japan and its use for tectonic synthesis. In J.R. Hein and J. Obradovic, Eds., Siliceous deposits of the Tethys and Pacific regions, p. 201–215. Springer, Berlin.

Heaney, P.J. (1993) A proposed mechanism for the growth of chalcedony. Contribution to Mineralogy and Petrology, 115, 66–74.

Heaney, P.J. and Davis, A.M. (1994) Geochemical self-organization in agates at the sub-micro scale. Geological Society of America Abstracts with Programs, 26, A-111.

———(1995) Observation and origin of self-organized textures in agates. Science, 269, 1562–1565.

Heaney, P.J. and Post, J.E. (1992) The widespread distribution of a novel silica polymorphs in microcrystalline quartz varieties. Science, 255, 441–443.

Heaney, P.J., Veblen, D.R., and Post, J.E. (1994) Structural disparities between chalcedony and macrocrystalline quartz. American Mineralogist, 79, 452–460.

Huston, T.J. and Walter, L.M. (1995) Kinetics of quartz precipitation at 180 °C: effects of NaCl and degree of quartz supersaturation. Geological Society of America Abstracts with Programs, 27, A-310.

Johnson, J.W., Oelkers, E.H., and Helgeson, H.C. (1992) SUPCRT92: a software package for calculation the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000 °C. Computers and Geociences, 18, 899–947.

Lund, E.H. (1960) Chalcedony and quartz crystals in silicified coral. American Mineralogist, 45, 1304–1307.

McLaren, A.C. and Phakey, P.P. (1966) Electron microscope study of Brazil twin boundaries in amethyst quartz. Physica status Solidi, 13, 413–422.

McLaren, A.C. and Pitkethly, D.R. (1982) The twinning microstructure and growth of amethyst quartz. Physics and Chemistry of Minerals, 8, 128–135.

Midgley, H.G. (1951) Chalcedony and flint. Geological Magazine, 88, 179–184.

Miehe, G. and Graetsch, H. (1992) Crystal structure of moganite: a new structure type for silica. European Journal of Mineralogy, 4, 693–706.

Miehe, G., Graetsch, H., and Flörke, O.W. (1984) Crystal structure and growth fabric of length-fast chalcedony. Physics and Chemistry of Minerals, 10, 197–199.

Rimstidt, J.D. and Barnes, H.L. (1980) The kinetics of silica-water reactions. Geochimica et Cosmochimica Acta, 44, 1683–1699.

Walther, J.V. and Helgeson, H.C. (1977) Calculation of the thermodynamic properties of aqueous silica and the solubility of quartz and its polymorphs at high pressure and temperature. American Journal of Science, 277, 1315–1351.

Wang, Y. and Merino, E. (1990) Self-organizational origin of agates: banding, fiber twisting, composition, and dynamic crystallization model. Geochimica et Cosmochimica Acta, 54, 1627–1638.

———(1995) Origin of fibrosity and banding in agates from flood basalts. American Journal of Science, 295, 49–77.

Wenk, H.-R., Shaffer, S.J., and Van Tendeloo, G. (1988) Planar defects in low temperature quartz. Physica Status Solidi (A), 107, 799–805.

Zhang, J.-W. and Nancollas, G.H. (1990) Mechanisms of growth and dissolution of sparingly soluble salts. In Mineralogical Society of America Reviews in Mineralogy, 23, 365–396.

MANUSCRIPT RECEIVED JANUARY 3, 1997
MANUSCRIPT ACCEPTED NOVEMBER 6, 1997
PAPER HANDLED BY RICHARD J. REEDER