INTRODUCTION

Natural gyrolite and other minerals in the CaO-SiO₂-H₂O (C-S-H) system occur in association with zeolites as low-temperature hydrothermal replacement products of basic and ultrabasic igneous rocks. Gyrolite was first discovered on the Isle of Skye, U.K., by Anderson (1851) who quoted a composition of Ca₅Si₆O₁₆(OH)₂·4H₂O. Subsequently it has been found at other localities, and has also been hydrothermally synthesized (Flint et al. 1938). The Ca/Si ratio quoted by Anderson was confirmed by later studies, but different values for the water content have been reported and a more reliable formula seems to be Ca₁₆Si₂₄O₆₀(OH)₈·14H₂O (Merlino 1988).

Disordered “C-S-H gel” of a similar composition to gyrolite is one of the major constituents of hydrated Portland cement and its formation plays an important role in the cement setting process (Taylor 1997). In recent years, environmental scientists have been studying the formation of C-S-H phases as it is thought that they will form, at elevated temperatures, in and around cementitious nuclear waste sites (Hodgkinson and Hughes 1999). Within this environment, disordered and crystalline C-S-H phases including gyrolite can be produced in several ways. The first is by direct interaction of ground waters with solidified high-level radioactive waste glass at high temperature (around 200 °C) under saturated vapor conditions. Above 200 °C, truscottite [Ca₉Si₁₆O₄₀(OH)₂·2H₂O] is the stable phase, although gyrolite can be metastably produced up to 270 °C. Below 120 °C, a poorly ordered C-S-H gel is produced, but this may be metastable with respect to gyrolite given a long enough synthesis time. Synthetic Z-phase [Ca₁₆Si₂₄O₆₀(OH)₈·14H₂O] can be produced by autoclaving either a C-S-H gel, or a mixture of lime and amorphous silica, at temperatures varying from 140 to 240 °C as an intermediate phase in the synthesis of gyrolite (Gard et al. 1975). No natural samples are known, although some gyrolite samples have been reported with small inclusions of intergrown Z-phase (Assarsson 1957). Despite all these studies, no detailed mechanistic or kinetic work has been reported on the hydrothermal formation of gyrolite.

This paper reports in situ studies of the hydrothermal formation of gyrolite at temperatures varying from 190 to 240 °C, utilizing a synchrotron source of high-energy X-rays and energy-dispersive powder diffraction (EDPD).

STRUCTURE AND STABILITY OF GYROLITE AND RELATED PHASES

Gyrolite was first synthesized by Flint et al. (1938) and subsequently by other researchers (Meyer and Jaunarajs 1961). It was reported to be stable between 120 and 200 °C under saturated water vapor pressure conditions. Above 200 °C, truscottite [Ca₉Si₁₆O₄₀(OH)₂·2H₂O] is the stable phase, although gyrolite can be metastably produced up to 270 °C. Below 120 °C, a poorly ordered C-S-H gel is produced, but this may be metastable with respect to gyrolite given a long enough synthesis time. Synthetic Z-phase [Ca₁₆Si₂₄O₆₀(OH)₈·14H₂O] can be produced by autoclaving either a C-S-H gel, or a mixture of lime and amorphous silica, at temperatures varying from 140 to 240 °C as an intermediate phase in the synthesis of gyrolite (Gard et al. 1975). No natural samples are known, although some gyrolite samples have been reported with small inclusions of intergrown Z-phase (Assarsson 1957). Despite all these studies, no detailed mechanistic or kinetic work has been reported on the hydrothermal formation of gyrolite.

The first structural analysis of gyrolite was performed by Mackay and Taylor (1953) who showed that gyrolite has a hex-

ARTICLES

In-situ synchrotron study of the kinetics, thermodynamics, and reaction mechanisms of the hydrothermal crystallization of gyrolite, Ca₁₆Si₂₄O₆₀(OH)₈·14H₂O

SAMUEL SHAW,* C. MICHAEL B. HENDERSON, AND SIMON M. CLARK†

Daresbury Laboratory, CLRC, Warrington WA4 4AD and Department of Earth Sciences, University of Manchester, Manchester M13 9PL, U.K.

ABSTRACT

The hydrothermal crystallization of gyrolite was studied dynamically at 190–240 °C using synchrotron-based in situ Energy Dispersive Powder Diffraction (EDPD). The reaction mechanism involves the initial crystallization of a calcium silicate hydrate (C-S-H) gel, which has a sheet structure with well ordered Ca(O,OH) layers and disordered silicate layers. This is followed by the intermediate formation of Z-phase which finally transforms to gyrolite. This process involves ordering of the silicate layers and an increase in the order along c.

Kinetics data for all stages of the crystallization process were determined by analyzing the growth and decline of various diffraction peaks with time. The activation energy (Ea) (nucleation) for Z-phase is ~39 kJ/mol while that for gyrolite is ~56 kJ/mol. Ea (crystallization) of gyrolite is higher at ~80 kJ/mol. The reaction occurs via a two-dimensional, diffusion-controlled mechanism and is a continuous process that suggests that Z-phase is an unstable, transient phase.

* Present address: Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305-2115, U.S.A. E-mail: sshaw@pangea.stanford.edu
† Present address: Lawrence Berkeley National Lab, 1 Cyclotron Road Mailstop 80-101, Berkeley, California 94720, U.S.A.