American Mineralogist, Volume 110, pages 699–708, 2025

Magnesite formation during nesquehonite decomposition in the presence and absence of retained self-generated gases and the role of X-ray amorphous materials as essential stores for CO_2

Bree Morgan[1,2,*,‡], Sasha Wilson[3,†], Ian C. Madsen[2], Yesim M. Gozukara[4], Justin A. Kimpton[5], and Helen E. Maynard-Casely[6]

[1]Geocoastal Research Group, School of Geosciences, The University of Sydney, Camperdown, Sydney, New South Wales 2006, Australia
[2]CSIRO Mineral Resources, Clayton South, Victoria 3169, Australia
[3]Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta T6G 2E3, Canada
[4]CSIRO Manufacturing, Clayton South, Victoria 3169, Australia
[5]Australian Synchrotron, ANSTO, 800 Blackburn Road, Clayton, Victoria 3168, Australia
[6]Australian Nuclear Science & Technology Organisation, New Illawarra Road, Lucas Heights, New South Wales 2234, Australia

Abstract

Long-term storage of CO_2 in nesquehonite ($MgCO_3 \cdot 3H_2O$) relies on its transformation to highly stable magnesite ($MgCO_3$) in a naturally occurring, centuries-long process. Here, we pair in situ X-ray diffraction (XRD) and thermogravimetric analysis to investigate the thermal transformation (30–650 °C, 5 °C/min) of nesquehonite to magnesite, under both open and closed experimental conditions in a supplied atmosphere of CO_2 or N_2, and the presence or absence of self-generated gases (i.e., CO_2, water vapor). We found that following the structural collapse of nesquehonite, magnesite only forms in the presence of gaseous CO_2, whether that be externally supplied or self-generated. This is consistent with a dehydration-crystallization mechanism, with increased local accumulation of CO_2 (and in a closed system, H_2O vapor) shifting thermal events to higher temperatures, allowing for the crystallization of magnesite. Approximately 20 wt% more magnesite formed when nesquehonite was flushed with CO_2 gas during heating in an open system, rather than held within a closed, static CO_2 atmosphere. We hypothesize that this difference is due to complete dehydration being more difficult to achieve in a closed system, delaying the crystallization of magnesite. Additionally, the distribution of passivating reaction products on unreacted mineral cores may occur in closed systems, where self-generated humidity is retained and the dissolution-precipitation of reaction products may occur at mineral surfaces. We also found that amorphous materials are dominant intermediate stores for CO_2, which is significant given they are not typically considered during carbon accounting in natural landscapes or engineered settings. We proposed a novel method to accurately quantify amorphous solids from XRD data during in situ studies where significant gas loss occurs. Our findings further our mechanistic understanding of how magnesite forms from crystalline and amorphous precursors under a range of environmental and industrial conditions, which is key to optimizing stable CO_2 storage in Mg-carbonate minerals. In particular, it highlights the importance of considering the role of amorphous phases, atmospheric composition, and self-generated gas retention during magnesite formation.

Keywords: Nesquehonite, amorphous, magnesite, carbon mineralization, in situ X-ray diffraction, thermal decomposition, Rietveld refinement, CO_2, water vapor