Crystal structure of B-gehlenite from an *in situ* XRPD study of datolite transformation upon heating

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Introduction and Experimental

Datolite, $CaBSiO_4(OH)$, belongs to the gadolinite group of minerals which have some petrological relevance in magmatic and hydrothermal environments as possible indicators of temperature and petrogenetic conditions. It has been reported that heating of datolite above 700°C in air leads to a dehydroxylated new phase which resembles a boron-containing analogue of gehlenite [1, 2]. However, due to the inferred metastable nature of boron-gehlenite derived from datolite and the unsuccessful attempts of synthesis [1], its atomic structure has never been reported yet.

We undertook a time-resolved X-ray powder diffraction (XRPD) study of the thermal behavior of datolite by collecting the *in situ* variable-temperature pattern in the range from RT to 925°C. Data were measured by a Translating Imaging Plate system at the BM08 beamline (GILDA) of ESRF. A series of intensity-2θ patterns, extracted from the variable-temperature image, was then Rietveld refined to obtain a continuous crystallographic picture of the thermal transformations and the complete description of the boron-gehlenite high-T phase.

Discussion of Results

The variable-temperature pattern shows that the high-T phase persists from the phase transition temperature, at about 750°C, up the upper limit of our experiment, 930°C.

The Rietveld refinement demonstrates that the high-T dehydroxilation product of datolite is a well crystallized boron-gehlenite, $Ca_2B_2SiO_7$, which conforms the space group $P\text{-}42_1m$. In agreement to what previously suggested [1, 2], the results show that Si and B are fully ordered in the two non-equivalent tetrahedral sites, T1 and T2, respectively and that the eight-fold coordination shell of calcium ions in B-gehlenite is retained very similar to that in parent datolite.

The comparison of thermal expansion of the unit cell parameters and the polyhedral volumes for both phases, datolite and boron-gehlenite, adds some information on the topotactic nature of their structural relationships.

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N_2O fluxes from coastal waters due to submarine groundwater discharge

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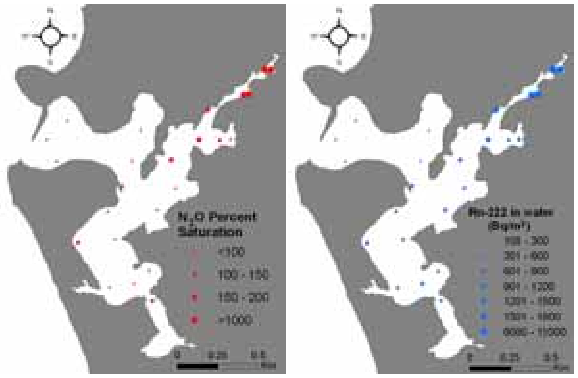
Nitrous oxide (N_2O), a greenhouse gas, is present at much lower atmospheric concentrations than CO_2. However, N_2O has ~300x the radiative forcing of CO_2 on a molar basis and a residence time in the atmosphere of ~ 100 years [1]. Hence, increases in N_2O concentrations will have an impact on future climate. Fluxes of N_2O from the coastal zone are probably significant to global budgets, but remain poorly quantified [2], as do the mechanisms driving important fluxes.

In this work we evaluated whether submarine groundwater discharge might contribute significant fluxes of N_2O to coastal waters and hence to the atmosphere. We carried out simulaneous measurements of ^{222}Rn, a tracer of groundwater discharge, and N_2O, in coastal embayments on Cape Cod (USA). Parallel patterns of enrichment of ^{222}Rn and N_2O strongly suggest a contribution of groundwater discharge to N_2O fluxes. N_2O concentrations as high as 1000% of saturation imply a large N_2O flux to the atmosphere (several hundred μmol $m^{-2}d^{-1}$). The relationship between N_2O and ^{222}Rn suggests the N_2O is produced either by nitrification or denitrification in nearshore sediments, although additional work is needed to distinguish between these possibilities.

Given the large flux of nutrients to coastal waters in many locations from groundwater [3], and given common travel times of years to decades between groundwater recharge and discharge to coastal waters, these data suggest that coastal groundwater discharge may continue to be a source of N_2O to the atmosphere for many years.



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