The nyerereite crystal structure: a possible messenger from the deep Earth.

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Abstract

Carbonates in the system Na$_2$CO$_3$–CaCO$_3$ are nowadays suggested as having a wide stability field at conditions of the mantle transition zone. The proposed analysis of nyerereite crystal structure, that have limited stability fields at ambient conditions, and its similarities with already known carbonates stable at high pressure conditions, allowed to propose that nyerereite likely undergoes phase transition at both high-pressure/high-temperature conditions supporting the hypothesis that it takes part in the carbon transportation from the mantle/deep crust towards the surface with important implication for the deep carbon cycle associated with carbonatites.

K-free nyerereite [Na$_2$Ca(CO$_3$)$_2$] was synthesized both at hydrothermal conditions and from the melt. The crystal structure of nyerereite was here refined as a three-component twinned structure in the centrosymmetric Pbca space group with ratio of the three twinning components 0.221(3):0.287(3):0.492(3). Twinning at micro- and nano- level can introduce some minor structural deformations that influence the likely occurrence of the inversion center as one of the symmetry elements in nyerereite crystal structure. Based on the automated topological algorithms we show that nyerereite has the unique crystal structure, not having analogues among the known crystal structures, except for the structure with similar composition K$_2$Ca(CO$_3$)$_2$ - fairchildite.

A comparison between the centrosymmetric Pbca nyerereite structure and that of aragonite (CaCO$_3$, Pmcn space group) is proposed and two main scenarios arises for the high pressure form of Na$_2$Ca(CO$_3$)$_2$: (1) polysomatic relations as the interlayering of the high pressure polymorph Na$_2$CO$_3$ and CaCO$_3$ - aragonite, and (2) high pressure crystal structure with 9-fold coordinated Na and Ca sites resembling that of aragonite. The proposed discussion heightens the interest in the baric behavior of the nyerereite structure and strengthens the hypothesis about the possibility for the nyerereite crystal structure to be stable at high pressure/high temperature conditions.
Keywords: Nyerereite, single-crystal X-ray diffraction, hydrothermal synthesis, melt crystallization, Raman spectroscopy, alkali-carbonates.

Introduction

The ubiquitous occurrence of Ca-Mg carbonates on Earth comes together with an intriguing paucity of alkaline and earth-alkaline carbonatites in the CaCO$_3$-(Na,K)$_2$CO$_3$ system likely due to their ephemeral behavior. Minerals such as nyerereite [(Na$_{1.64}$K$_{0.36}$)Ca(CO$_3$)$_2$ (Bolotina et al., 2017)] and gregoryite [(NaCa$_x$K$_{2-x}$CO$_3$], at ambient conditions and in presence of meteoric water, rapidly transforms to the end-members Ca-carbonatite rocks (Gavryushkin et al, 2016), through intermediate stages such as pirssonite-like structures [Na$_2$Ca(CO$_3$)$_2$·2(H$_2$O)] (Zaitsev and Keller, 2006; Zaitsev et al., 2008; Stoppa et al. 2009 and references therein). The transformation is quite rapid, occurring over a few months to a couple of years (Zaitsev and Keller, 2006).

Alkali-carbonates in the geological record

Alkaline carbonatite magmas are of great interest because they may represent partial melts produced at significantly lower mantle melting temperatures compared with basaltic magmas (e.g. Golubkova et al. 2015) and they may represent a powerful agent promoting mantle metasomatism (Rosatelli et al., 2007). Different geological settings host carbonatites, including intra-plate magmatism in continental areas and along continental rifts (Mattsson et al. 2018 and references therein) raising important questions on the geodynamic significance of carbonatite magmatism.

The only active carbonatite volcano on the Earth, erupting significant amount of natrocarbonatite magmas (Na$_2$O + K$_2$O ~ 40 wt%, Keller and Zaitsev, 2012), is the Oldoinyo Lengai volcano (East African Rift System, northern Tanzania). The erupted products are
predominantly composed of phonolitic and nephelinitic pyroclasts and lesser amounts of lava flows (Mattsson et al. 2018). The carbonatite lavas present the lowest temperature (>600 °C) and the lowest viscosity (Krafft and Keller, 1989; Dawson, et al., 1990; Oppenheimer, 1998) and the main rock-forming minerals of these natrocarbonatites are (orthorhombic) nyerereite and gregoryite (e.g. McKie and Frankis, 1977; Peterson, 1990; Zaitsev et al., 2009; Mitchell and Kamenetsky, 2012).

One of the most interesting occurrences of Na-Ca carbonates is in mantle-derived melt inclusions, which pose important constraints to the composition and origin of kimberlites and mantle-derived melts and provide information on the nature of primary melts and deep Earth composition (Sharygin et al., 2017; Giuliani et al., 2020).

Nyerereite-like carbonates were identified as daughter minerals within primary/secondary melt inclusions in rock-forming minerals of kimberlites from Udachnaya-East, Gahcho Kué, Jericho, Aaron, Leslie, Koala, Roger, Monastery, Bultfontein pipes, Majuagaa dike, Mark kimberlite hypabyssal body and Benfontein kimberlite sill complex (e.g. Golovin et al., 2003, 2007, 2017a; Kamenetsky et al., 2009, 2013; Giuliani et al., 2017; Abersteiner et al., 2018a, 2018b, 2019, 2020). These kimberlite emplacements are located practically within all worldwide ancient cratons. Moreover, nyerereite-like carbonates were found among the daughter minerals within high-pressure mantle origin primary/secondary carbonatite melt inclusions in minerals of the mantle xenoliths from kimberlites Bultfontein and Udachnaya-East pipes (Giuliani et al., 2012; Golovin et al., 2017a, 2018, 2020) and even as minerals from multiphase solid inclusions in diamonds from the Juina area, Brazil (Kaminsky et al., 2009).

A further example is the kamaflugite-melilitite-carbonatite lime-rich igneous rocks outscopping in the italian Umbria-Latium ultra-alkaline province and the Intramontane Ultra-alkaline province (Panina et al., 2003; Isakova et al., 2017; Isakova et al., 2019). In this area, nyerereite, in the form of crystalline inclusions, was identified in the minerals of rocks from Vulture
Nyerereite is also present as a daughter mineral within melt inclusions in minerals from the Gardner and Kovdor carbonatite-bearing ultramafic alkaline complexes (Veksl er et al., 1998; Sokolov et al., 2006), calcite-rich carbonatites from the Oka carbonatite complex (Chen et al., 2013), carbonatitic lavas in Catanda (Campeny et al., 2015) and calciccarbonatite and jacupirangite from Kerimasi volcano (Guzmics et al., 2011; Káldos et al., 2015).

Nyerereite crystal structure and open questions

The crystal structure solution of nyerereite has been the subject of several studies (e.g. Frankis and McKie 1973, Gavryushkin et al. 2016, Bolotina et al., 2017). Difficulties in the final solution of the nyerereite crystal structure were overcome by using K-free synthetic samples (Frankis and McKie, 1973; Gavryushkin et al., 2016; Song, 2017) where incommensurate modulation is not present (Frankis and McKie, 1973; Gavryushkin et al., 2016; Bolotina et al., 2017). Synthetic nyerereite showed good crystallinity and the crystal structure was refined as a three-component orthorhombic twins with either \( P2_1\text{ca} \) (Gavryushkin et al., 2016) (Figure S1 deposited in the Supplemental Materials section) or \( P\text{bca} \) (Song et al., 2017) space groups (Figure S2 deposited in the Supplementary Materials section). Two high temperature phase transitions were observed in nyerereite starting from the room temperature structure (\( \alpha \)-nyerereite) towards (i) \( \beta \)-nyerereite (\( C\text{mcm} \) space group; Gavryushkin et al., 2016) in the \( T \) range 292°C (natural sample) - 400°C (synthetic sample) and (ii) \( \gamma \)-nyerereite (\( P6_3/mmc \) symmetry; Gavryushkin et al., 2016) in the \( T \) range 340°C (natural sample) - 445°C (synthetic sample) (Johnson and Robb, 1973; Evans and Milton, 1973; McKie and Frankis, 1977).
Analogously to fairchildite [high $T$ form of $K_2Ca(CO_3)_2$], oxygens in $\gamma$-nyerereite are expected to be disordered (Gavryushkin et al., 2016; Pertlik, 1981).

Besides the hydrothermal synthesis, other techniques have been adopted to synthesize $Na_2Ca(CO_3)_2$ crystals, namely, thermally induced solid-state reaction of $Na_2CO_3 + CaCO_3$ (Smith et al., 1971) and dehydration of mineral gaylussite [$Na_2Ca(CO_3)_2\cdot5(H_2O)$] (Evans and Milton, 1973; Johnson and Robb, 1973).

In the present work we consider different synthesis conditions, namely hydrothermal synthesis and synthesis from the melt, the latter one employed to obtain a new type of nyrereite samples that resembles the natural samples observed in melt inclusions of kimberlites. The synthetic alkali-carbonates mixtures are studied by a multimethodological approach, namely, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), Raman spectroscopy and single crystal X-ray diffraction (SC-XRD) with a particular focus on the structure solution of nyrereite, showing that it can be centrosymmetric or not, depending on conditions of crystallization.

Despite the well-known high-pressure behavior of Ca-Mg-Fe carbonates(e.g., Zucchini et al., 2014, 2017; Merlini et al., 2012, 2016; Cerantola et al., 2017), the Na-Ca phase stability at mantle/deep crust conditions is poorly known and experimental and theoretical studies have been limited to minerals other than nyrereite (Borodina et al., 2018; Vennari et al., 2018; Rashchenko et al., 2020). The only exception is the high-pressure (HP) Raman study of nyrereite made by Rashchenko et al. (2017) where, however, the analyzed $P$ range (up to 6.4 GPa) and the lack of crystal structure data did not allow the characterization of the minor structural observed deformations that occurred at 0.5 and 3.0 GPa, that were speculatively ascribed to rearrangement of the $CO_3^{2-}$ groups in the nyrereite crystal structure.

The proposed analysis of nyrereite crystal structure, that have limited stability at low pressures and temperatures, and the study of its similarities with already known carbonates, stable at HP...
conditions, allowed to propose that nyerereite likely undergoes phase transition at both HP and high-temperature (HT) conditions that could stabilize them down to the mantle transition zone, supporting the hypothesis that these minerals take part in the carbon transportation from the mantle/deep crust towards the surface with important implication for the deep carbon cycle associated with carbonatites.

Materials and methods

Synthesis

Hydrothermal synthesis. Hydrothermal synthesis of nyerereite was performed, following the procedure described in Frankis and McKie (1973), in water-pressurized cold seal pressure vessels (Nimonic 105) at the Department of Geology at University of Camerino (Italy). The starting material was prepared from a mixture of dried carbonates, Na$_2$CO$_3$ (60 mole%) and CaCO$_3$ (40 mole%). The mixture was first homogenized and mixed in an agate ball mill for 30 min before the capsule preparation. The powder material (~15 mg per experiment) along with ca. 10 ml of distilled water was then loaded into Au capsules (with dimensions of 25 mm length, 3 mm inner diameter, 3.4 mm outer diameter). The capsules were weighed after each addition of material and then sealed by welding. Weight after welding was checked to verify that water was not lost during welding. The intrinsic redox condition of the CSPV apparatus is close to NNO +0.8 (Di Matteo et al., 2004; Fabbrizio et al., 2006; Fabbrizio and Carroll, 2008; Stabile et al., 2018, 2020). Temperature was measured in the sample position with a K-type thermocouple with an accuracy of ±5°C. Pressure was monitored by a high-pressure transducer or Bourdon-tube pressure gauges, considered accurate to ±2 MPa (Arzilli et al., 2020). The samples were heated and pressurized to reach the experimental temperature of 550°C and pressure of 100 MPa. Experiments lasted 15 days (hereafter NHD15) and the samples were
quenched from experimental conditions to room conditions by removing the bomb from the furnace and immersing it in a high-pressure stream of compressed air, providing a cooling rate of \(~120^\circ\text{C/min.}\) For all the samples run, the quench was isobaric as pressure was maintained constant during cooling by using a large volume pressure reservoir and a hand operated pressure generator.

**Synthesis from the melt.** \(\text{Na}_2\text{Ca(CO}_3\text{)}_2\) crystals (hereafter NMAG) were obtained by slow cooling of the stoichiometric melt in a vertical vitreous graphite crucible. The crucible with a mixture of \(\text{CaCO}_3\) and \(\text{Na}_2\text{CO}_3\) was placed in a quartz reactor, which was continuously purged with nitrogen gas. Heating was carried out by a resistive heating furnace up to \(850^\circ\text{C.}\) There was a minimum temperature at the crucible's bottom, which ensured directional crystallization from bottom to top with a decrease in temperature at a rate of \(1\) deg/hour.

**SEM – EDS**

Analyses were obtained at the Analytical Centre for Multielemental and Isotope Research of Siberian Branch of the Russian Academy of Science (Sobolev Institute of Geology and Mineralogy, Novosibirsk, Russia). The analyses of hydrothermal and magmatic synthetic nyerereite and back-scattering electron (BSE) images were obtained by a Tescan MIRA3 LMU scanning electron microscope equipped with an Aztec Energy X-Max 50+ energy-dispersive X-ray microanalysis system. An accelerating voltage of \(20\) keV and a beam current of \(1.44\) nA were used. Spectrum acquisition live time was \(35\) s. Matrix correction was performed with the XPP algorithm. Pure cobalt was measured to control the probe current and the energy shift.

**Raman spectroscopy**

Raman point measurements (from \(0\) to \(4000\) cm\(^{-1}\)) of individual grains and mixtures of compounds were performed using a LabRAM HR800 dispersive Raman spectrometer using
the excitation line of a 532-nm Nd:YAG laser. In all measurements, a laser power of approximately 10 mW was employed. The scattered Raman light was analyzed with a CCD detector after being dispersed by a grating of 1800 grooves mm\(^{-1}\). A 100× lens with a numerical aperture of 0.9 was used on a BX-51 microscope. The frequency was calibrated using the first-order Si line at 520.6 cm\(^{-1}\). The wavenumbers are accurate to ±1 cm\(^{-1}\).

In experiments on nyerereite synthesized from the melt, single crystals were cut and polished in one direction, therefore, they have the same spectra (the same ratio of the intensity of the Raman lines relative to each other) at different points of the sample.

**SC-XRD**

Optically clear single nyerereite crystals (approximately 20x20x50 \(\mu\)m\(^3\) in NMAG and 50x50x100 \(\mu\)m\(^3\) in NHD15) were separated from the synthesis run products and analyzed at room temperature at the University of Perugia (Italy) by using an Oxford Diffraction Xcalibur diffractometer with CCD detector and MoK\(\alpha\) radiation (\(\lambda = 0.7107\ \text{Å}\)). Detector distance to the sample was ca. 66 mm with pixel size ca. 60 \(\mu\)m.

Rotation pictures and 360° \(\phi\)-scans allowed us to control the crystal quality and optimize the data collection parameters, respectively. Measurements were carried out in a \(\omega\)-scan mode with 1.0° scan width and 15 s exposure time. The resolution of data collection was set to \(\sin{\theta}/\lambda = 0.72\ \text{Å}^{-1}\).

Data reduction was performed by means of CrysAlisPro software (Agilent Technologies UK Ltd, Yarnton, England.) and an empirical absorption correction was applied by the ABSPACK module as implemented in CrysAlisPro software (Oxford Diffraction/Agilent Technologies).

Refinements were carried out by means of the SHELXL (Hübschle et al., 2011) in both \(P2_1ca\) and \(Pbca\) space groups, with anisotropic displacement parameters. In Figure S3 (Supplemental materials), the collected data extraction and the unit cell used for reflection indexing are shown.
together with the evidence of the three-component domains rotated of ca. 120° around the c axis.

In both space groups twinning was introduced following the twinning matrix:

\[
\begin{bmatrix}
-\frac{1}{2} & 1 & 0 & -\frac{3}{4} & \frac{1}{2} & 0 & 0 & 0 & 1
\end{bmatrix}
\]

**Topological analysis**

The topological analysis was performed by means of ToposPro (http://topospro.com), with the aim to search for the topological analogues of the nyerereite crystal structure, through the whole Inorganic Crystal Structure Database (ICSD, release 2020/2) (Blatov et al., 2014). Hereafter, we use three-letter bold symbols of the Reticular Chemistry Structure Resource nomenclature (see Reticular Chemistry Structure Resource at http://rcsr.anu.edu.au/) (O’Keeffe et al., 2008) or ToposPro NDk-n symbols (Alexandrov et al., 2011) to designate the topological types of the underlying nets. Further details on the used procedure are given in the Supplementary material section together with the obtained results.

**Results**

The synthesis experiments performed in this work were successful and we were capable of recovering several milligrams of sample from each experiment. The run products coming out from the hydrothermal samples have already been characterized by Fastelli et al. (2021).

Reflected light images and backscattered electrons (BSE) images of the NHD15 and NMAG samples are shown in Figure 1 and Figure 2 where the lightest regions were attributed, by means of SEM-EDS chemical analysis, to nyerereite with averaged chemical formula Na_{1.996(5)}Ca_{1.017(3)}(CO_3)_2 and Na_{1.996(7)}Ca_{1.002(4)}(CO_3)_2 for NHD15 and NMAG, respectively. The single point chemical analyses are given in the Supplemental Material sections as Table S1. The dark portions in Figures 1 and 2 are attributed to a mixture mainly consisting of Na_2CO_3.
(Figure 2), with minor amounts of Na-Ca carbonates, together with unreacted CaCO₃ grains in NMAG. In Supplemental material section backscattered electrons (BSE) images and EDS X-ray maps recorded on selected portions of NMAG and NHD15 are given (Figure S4).

The synthesis run products showed the occurrence of differently shaped nyerereite crystals. On the one hand, NMAG shows acicular nyerereite crystals ranging from a few microns up to a few tens of microns (Figure 2a), strongly interconnected with the Na₂CO₃ matrix. On the other hand, in NHD15, nyerereite appears as globular aggregates of rounded crystals with maximum dimensions of approximately 120-150 μm (Figure 2b).

Syntheses products

Raman spectra for individual differently oriented nyerereite grains were collected in the range from 0 to 2000 cm⁻¹. No differences were observed by comparing them with Golovin et al. (2017b) data (Figure 3), showing the highest peaks at 1073 and 1087 cm⁻¹ (± 1 cm⁻¹).

Besides the occurrence of nyerereite, additional signals are present in the NHD15 and MNAG Raman spectra (Figure 4). A strong line at 1070 cm⁻¹ is present in both NHD15 and NMAG (Figure 4c) that might be related to the presence of thermonatrite (Na₂CO₃·H₂O) together with the peaks at 687 cm⁻¹ + 702 cm⁻¹ (Figure 4b) and 2972 cm⁻¹ + 3254 cm⁻¹ (Figure 4d) (Jentzsch et al. 2013, Frezzotti et al. 2012, Frost et al. 2009) in agreement with results from Fastelli et al. (2021). Additional peaks occur at 1079 cm⁻¹ + 1082 cm⁻¹ (Figure 4c) as well as at 699 cm⁻¹ (Figure 4b) that can be attributed to the γ-Na₂CO₃ phase (Shatskiy et al., 2013, 2015), whose presence was also observed by Gavryushkin et al. (2016) and Fastelli et al. (2021) in their synthesis run products.

An unassigned peak at approximately 134 cm⁻¹ in Figure 4a belongs neither to any of the likely occurring phases (nyerereite, γ-natrite, thermonatrite), nor to plausible occurring phases in the Na₂CO₃ – CaCO₃ series checked by a comparison with data stored in the RUFF database.
(Lafuente et al. 2016) as well as with data from literature (Golovin et al. 2017b). Thus, this might be the signal that an unknown phase in the Na₂CO₃ – CaCO₃ series is present in the synthesized sample. However, given the very fine intergrowth of the additional phases with Na₂Ca(CO₃)₂ in the mix region (Figure 2), it is impossible to get both SC-XRD and Raman spectra from the individual grain. Further studies are needed to truly define the phase assemblage present in the mix region, but is beyond the scope of the present work.

Nyerereite structure

The nyerereite structure refinements in both $P2_1ca$ and $Pbca$ space groups were satisfactory in terms of the agreement parameters R1 (<0.07) and wR2 (<0.16) as well as GooF (~1). A three-component twinned structure rotated of ca. 120° around the c axes was refined in both space groups. However, in $P2_1ca$ too many correlations between atomic coordinates were observed, meaning that corresponding atoms are symmetry equivalent. Thus, we can definitely recommend $Pbca$ as the space group for both hydrothermal and magmatic nyerereite, in agreement with results of Song et al. (2017). The ratio of the three twinning components is refined as 0.221(3):0.287(3):0.492(3). The details of data collection and refinement, together with the crystal structure data, can be found in the CIF file (deposited) for both HND15 and NMAG samples. Bond lengths and polyhedral volumes are given in Table S2 as Supplemental Material.

In Gavryushkin et al. (2016), where a different hydrothermal synthesis was proposed (partial replacement of Na₂CO₃ with NaOH as starting materials), a higher number of reflections broke the reflection conditions of $Pbca$ space group in their hydrothermal synthetic samples, with respect to the non-centrosymmetric space group $P2_1ca$. The refined ratio of the twin components showed a nearly identical amount being 0.3363(4):0.3446(4):0.3191(4). Thus, the observed difference in space groups is not an artefact of the refinement, but shows real
difference in the crystal structures, attributed to the different growth conditions, suggesting that
nyerereite can have different space groups and twinning at micro- and nano-level, which can
introduce some minor structural deformations that inhibit the occurrence of an inversion center.

**Topological analysis.** Our topological analysis suggests that nyerereite is characterized by a
unique topology, which does not have analogues in ICSD database except for the structure with
similar composition K₂Ca(CO₃)₂ (fairchildite), although the subnets of the separate atoms
constituting the structure are relatively widespread among carbonates and carbides. 738 crystal
structures of borates with stoichiometry similar to that of nyerereite were found in ICSD,
however they are all quite different from nyerereite. Among four double carbonates in the
system Na₂CO₃-CaCO₃ [nyerereite, shortite, Na₂Ca₃(CO₃)₄ and Na₄Ca(CO₃)₃], only
Na₂Ca₃(CO₃)₄ (Gavryushkin et al, 2014) and Na₄Ca(CO₃)₃ (Rashchenko et al, 2018) have
analogues among borates. Detailed results of the topological analysis of nyerereite are given in
the *Supplemental Material* sections.

**Polyhedra distortion and bond-valences calculation.** The polyhedral distortion index (D)
(Table S2, *Supplemental material*) and the bond valence sum (BVS) (Table S3, *Supplemental
material*) calculated following the values given by Brese and O’Keeffe (1991) were obtained
based on bond lengths as defined by Baur et al. (1974) and implemented using the open-source
crystallographic software VESTA (Momma and Izumi, 2011). As regards the carbonate group,
on the one hand, the pseudo-planar triangle in C1 is quite regular with the three bond-valences
that almost equal each other as in aragonite. The bond-valence of the three carbonate-oxygen
bonds has values in the range 1.32-1.34 both in aragonite and nyerereite with coefficient of
variation (CV), *i.e.* ratio of the standard deviation to the mean, of approximately 1-2% and a
device from planarity of 1.9° in NHD15 and 1.2° in NMAG (Table S2).
As regards the C2 site, the bond valences of the three (C-O) bonds are in the range 1.30-1.38
(CV ~ 3%) and the deviation from planarity is 3.2° in NHD15 and 2.5° in NMAG. The (C2-
O4) bond-valence is the highest (1.38) with respect to the other C-O bonds likely due to the high strength of the (Na1-O4) bond (bond valence = 0.22) and the low strength of both the (Na2-O6) and (Na1-O5) bonds being the bond valence 0.16 and 0.05, respectively. Figure 6 shows the atomic structure and bond length/strength.

Discussion

In all experiments, in addition to the “pure” Na$_2$Ca(CO$_3$)$_2$ nyerereite, a mixture consisting mainly of thermonatrite and γ-Na$_2$CO$_3$ was observed. In the Na$_2$CO$_3$:CaCO$_3$ range tested by our experiments (Na$_2$CO$_3$:CaCO$_3$ = 0.6:0.4 in NHD15, Na$_2$CO$_3$:CaCO$_3$ = 0.7:0.3 in NMAG), results are in agreement with Cooper et al. (1975). Given the ephemeral behavior of both natrite and nyerereite, the occurrence of anhydrous/hydrated Na$_2$CO$_3$ is not surprising and likely due to the interaction with atmospheric humidity and the handling during sample preparation that led to the formation of Na$_2$CO$_3$·H$_2$O. However, the crystal structure of nyerereite in both NHD15 and NMAG syntheses was here well refined as a three-component twinned structure in the centrosymmetric Pbca space group.

The performed topological analysis indicates that there are no strict analogies between the crystal structure of nyerereite and other carbonates except for the structure with similar composition K$_2$Ca(CO$_3$)$_2$ (fairchildite). In addition, we observe that double carbonates with simple stoichiometry as nyerereite (Na$_2$CO$_3$*CaCO$_3$) have no analogues among borates. However, an interesting comparison between the crystal structure of the centrosymmetric Pbca nyerereite structure and that of aragonite (CaCO$_3$, Pmcn space group) is proposed (Figure 7). The $a$ and $c$ axes are doubled in nyerereite with respect to aragonite ($a = 4.96$ Å, $b = 7.97$ Å, $c = 5.74$ Å; Antao and Hassan 2009), due to the presence of Na in the mineral crystal structure with the consequent inclination of the C(2)O$_3^{2-}$ groups, lying in the cavities occurring between two Na-layers, of approximately 58° with respect to the (ab) plane. A second set of carbonate
groups \([\text{C}(1)\text{O}_3^{2-}]\) lie in the \((ab)\) plane, parallel to the Ca-layer, and is less distorted with respect to the former \((D_{C1} = 0.002 - 0.004 \text{ and } D_{C2} = 0.004 - 0.006, \text{ Table } S2)\). The Ca polyhedra in nyerereite has a distortion index close to that of aragonite \((D_{\text{Ca-nyerereite}} = 0.03, \text{ Table } S2; D_{\text{Ca-aragonite}} = 0.025; \text{ Antao and Hassan, 2009})\). Notwithstanding the bond-valence requirements are respected in the \(Pbca\) nyerereite (Table S3 in \textit{Supplemental material}) with the bond length scheme previously defined by Gavryushkin et al. (2016), the observed differences in the bond-strengths within Na1 and Na2 polyhedra give rise to their observed higher distortion with respect to the Ca polyhedron \((D_{\text{Na-nyerereite}} = 0.05-0.07, \text{ Table } S2)\) as well as to the marked deviation from planarity of the C2 atom and tilting of the C(2)O\(_3^{2-}\) groups.

By the presented scenario, both Na1 and Na2 polyhedra are supposed to regularize with increasing pressure by likely including in their geometry additional oxygens and increasing their coordination number according to Prewitt and Downs (1998), as already observed in both carbonate and non-carbonate minerals, e.g., dolomite \([\text{CaMg(CO}_3\text{)}_2]\) (Merlini et al., 2012; Zucchini et al., 2014) and galenobismutite \((\text{PbBi}_2\text{S}_4)\) (Comodi et al. 2019). This could drive the \(Pbca\) nyerereite towards a crystal structure with 9-fold coordinated Na and Ca sites resembling that of aragonite at elevated pressure.

A second scenario might be proposed, based on the polysomatic relation of \(\text{Na}_2\text{Ca(CO}_3\text{)}_2\) structures with the structures of \(\gamma\)-\(\text{Na}_2\text{CO}_3\) and \(\text{CaCO}_3\) calcite (Bolotina et al, 2017). We suggest that some similar polysomatic relations will be preserved in the HP from of \(\text{Na}_2\text{Ca(CO}_3\text{)}_2\) and it can be presented as the interlayering of HP polymorphs \(\text{Na}_2\text{CO}_3\cdot P2_1/m\) (Gavryushkin et al. 2016, 2019) and \(\text{CaCO}_3\) in the form of aragonite. It is worth noting that aragonite was found as an inclusion in mantle olivine from carbonatite tuffs in a leucitite lava flow in Calatrava (Spain) providing evidences for a likely sublithospheric mantle origin for alkaline ultramafic magmas and extrusive carbonatites (Humphreys et al., 2010). The solubility of Na in the structure of...
Aragonite might be drastically increased through the formation of nano lamellae of HP polymorph of Na$_2$Ca(CO$_3$)$_2$ giving rise to what has been recently called “Na-aragonite” (Rashchenko et al., 2020). Our hypothesis about formation of modular structures between the HP form of Na$_2$CO$_3$ and aragonite at HP is supported by the amount of dissolved Ca$^{2+}$ in the structure of Na$_2$CO$_3$ up to 15% (Podborodnikov et al., 2018), which cannot be explained with isomorphism as the authors suggested.

The proposed hypotheses are consistent with recent studies on the HP behavior of Na-Ca carbonates (Grassi and Schmidt, 2011; Kiseeva et al., 2013; Litasov et al., 2013 Borodina et al., 2018; Vennari et al., 2018; Rashchenko et al., 2020) that have already suggested an important variety of Na-Ca double carbonates in the system Na$_2$CO$_3$–CaCO$_3$ at HP-HT, linked each other by a sequence of decomposition reactions (Rashchenko et al., 2020), as well as the existence of high-pressure polymorphs of Na$_2$Ca$_2$(CO$_3$)$_3$-shortite. As a consequence, the stability/decomposition reactions occurring in the mentioned phases during decompression are a fundamental constraint for the CO$_2$ release from mantle-derived magma, which can be expected to influence magma viscosity and eruption explosivity (Allison et al., 2021). If confirmed, the proposed scenarios might confer a role to nyerereite in the carbon transportation within the Earth’s mantle, and from mantle to shallow depths within the crust.

Further studies are necessary in order to determine the structure and phase stability of nyerereite and related phases at HP/HT conditions.

**Implications**

Our investigation helps to diagnose natural and synthetic alkaline and earth-alkaline carbonates by deciphering the structural characteristics of pure synthetic nyerereite with respect to natural samples. The accurate knowledge of the crystal structure of nyerereite allows us to speculate on its behavior at non ambient conditions, thus opening the possibility of a scenario where the
mineral has a wide stability field at pressure conditions higher than those applied during the synthesis experiments (100 MPa), consistent with HP experiments in the carbonate-silicate systems that revealed a number of Na-Ca carbonates resembling stoichiometries of Na$_2$Ca(CO$_3$)$_2$-nyerereite, Na$_2$Ca$_2$(CO$_3$)$_3$-shortite and Na$_2$Ca$_4$(CO$_3$)$_5$-burbankite (e.g., Kiseeva et al., 2013; Litasov et al., 2013; Thomson et al., 2016; Vennari et al., 2018; Rashchenko, 2020). Stabilization of Na-Ca carbonates at deep crust/mantle conditions, likely down to deep upper mantle and transition zone conditions, may have important implications for the solidus temperatures and formation of sodic dolomitic carbonatite melts and, in turn, the inner dynamic of the Earth. In fact, if at low pressure these melts are efficient transport agents of carbon from upper mantle to the crust due to their very low magmatic temperature and viscosity, at higher pressure we might expect changes in the carbonatitic minerals crystal structure also reflecting in changes in melt properties, e.g. density and viscosity, that might influence the mobility of carbonate melts in the deep upper mantle / transition zone. Nyerereite, then, may be claimed as another carbonate mineral responsible for the storage of carbon in the deep Earth and its mobility from the mantle, or the deep crust, to the surface. This may have significant implications for the deep carbon cycle associated with carbonatites.
Acknowledgements

The experiments were performed thanks to the financial program of the Department of Physics and Geology of the University of Perugia (“Fondo ricerca di Base 2018”; Principal Investigator AZ) and MIUR (project no. PRIN2017-2017LMNLAW “Connect4Carbon”).

PNG, AVG, KK and AK were supported by the state assignment project of Sobolev Institute of Geology and Mineralogy SB RAS.

MC wishes to thank all the members of the Italian School of Paleoanthropology and of the Tanzania Human Origins Research (THOR) project (www.thorproject.it).

MRC acknowledges laboratory support from PRIN2017-2017J277S9.

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Figures captions

**Figure 1.** Reflected light microscope images of NMAG (a, b) and NHD15 (c, d). Magnifications are 4x (a, c) and 20x (b, d).

**Figure 2.** Backscattered electron images showing products of experiments NMAG (a), NHD15 (b).

**Figure 3.** Comparison of the position of strong Raman lines for three separate grains of different orientations, obtained in the NHD15 experiments (top) as compared with spectra from Golovin et al. (2017) (bottom).

**Figure 4.** Raman spectra of the mixed areas, divided in four regions where the most intense Raman signals due to \( \text{CO}_3^{2-} \) vibrations are present (after Golovin et al., 2017b; Vennari et al., 2018): (a) spectral region where vibrations are due to the interaction between carbonate groups and Na-Ca sublattices, (b) spectral region that shown the \( \nu_4(\text{CO}_3^{2-}) \) (in-plane bending) vibrations, (c) spectral region where the \( \nu_1(\text{CO}_3^{2-}) \) (symmetric stretching) vibrations lie, and (d) water spectral region. Colors are attributed according to the legend shown in (a). Solid line spectra are the collected Raman spectra in the present work. The dashed dark red spectra are Raman data collected in three nyerereite crystals from Golovin et al. (2017b). Vertical lines represent the position of the Raman signals in reference data as follows: dotted orange is \( \gamma^- \)-Na\(_2\)CO\(_3\) (Shatskiy et al., 2015) and dashed red is thermonatrite (Jentzsch et al., 2013; Frezzotti et al., 2012). The arrow in a) shows the position of the unassigned signal.

**Figure 5.** CaCO\(_3\) (top left) and Na\(_2\)CO\(_3\) layers (top right) constituting nyerereite crystal structure and their superimposition in nyerereite crystal structure (bottom). Ca, Na, C(1)O\(_3\) and C(2)O\(_3\) atoms are colored in blue, yellow, dark brown and light brown, respectively.

**Figure 6.** Representation of a portion of the nyerereite unit cell content where selected atomic sites are shown for the Na1 and Na2 in yellow, Ca in blue, C1 in dark brown and C2 in light
brown. A schematic representation of the bond length for the O4, O5 and O6 atoms bonding C2 is illustrated being the sawtooth and the dashed lines the highest the lowest bond-valences, respectively.

**Figure 7.** Crystal structure of (a) nyerereite and (b) aragonite in the (ab) plane. Aragonite is shown in the $2 \times 1 \times 2$ supercell to highlight the similarities with nyerereite. Colors are as follows: yellow is Na; blue is Ca; red is O; dark and light brown are C1 (in nyerereite and aragonite) and C2 (in nyerereite), respectively. Figures were made by VESTA software (Momma and Izumi, 2011).
Figure 1b
Figure 1c
Figure 2a
Figure 3
Figure 4a
Figure 4b

Raman Intensity a.u.

Raman shift (cm$^{-1}$)

687 cm$^{-1}$

699 cm$^{-1}$

702 cm$^{-1}$
Figure 4c
Figure 4d

Raman shift (cm$^{-1}$)

Raman Intensity a.u.

2972 cm$^{-1}$

3254 cm$^{-1}$
CaC(1)O₃ layers with \textbf{hcb} topology

Na₂C(2)O₃ layers with \textbf{kgd} topology

crystal structure of nyerereite
with 5,6,8,9T2 topology

Figure 5
Figure 6