Polymerization of CO$_4$ groups in carbonates

L. Bayarjargal$^1$, D. Spahr$^1$, J. König$^1$, V. Milman$^2$, B. Winkler$^1$

$^1$Institute of Geosciences, Goethe University Frankfurt - Frankfurt am Main (Germany), $^2$Dassault Systèmes BIOVIA - Cambridge (United Kingdom)

Abstract
The building blocks of ‘conventional’ carbonates such as calcite or magnesite are trigonal planar [CO$_3$]$^{2-}$-groups [1,2]. These CO$_3$-groups remain stable as isolated groups up to pressures of ~70 GPa. At higher pressures and high temperatures above ~2000 K the formation of [CO$_4$]$^{4-}$-groups was observed and explained by the formation of carbon with sp$^3$-hybridized orbitals [2]. In contrast to sp$^2$-hybridized CO$_3$-groups, CO$_4$-groups may polymerize based on half-occupied orbitals that allow for additional bonding. However, extensive investigation of the polymerization of CO$_4$-groups was hindered by experimental difficulties to achieve such extreme conditions. In contrast to CO$_4$-groups, polymerizations of other orthoanions [MO$_4$] have been extensively investigated in the past. [SiO$_4$]$^{4-}$-tetrahedra are the main building blocks in silicates and play a major role in crystallography and mineralogy [3,4]. Tetrahedral SiO$_4$-groups can polymerize and build pairs, chains, rings, sheets or networks [3,4]. In addition to the SiO$_4$-tetrahedra in silicates, further anions such as [BO$_4$]$^{5-}$ -groups of borates are key-components in basic chemistry and polymerize with BO$_4$-groups and even with other BO$_3$ building blocks [5].

Recently, we demonstrated the synthesis of carbonates containing CO$_4$-groups at moderately high pressures (20-30 GPa) by reacting carbonates with either oxides or CO$_2$ [6-8]. These carbonates have chemical compositions other than the well-known ‘conventional’ carbonates (MeCO$_3$) and are either enriched in a metal oxide or CO$_2$ [6-8]. Some of them can even be recovered at ambient conditions [6,7]. The favorable synthesis pressure conditions allowed us to investigate different structural aspects and the polymerization of CO$_4$-groups in large detail. As a result of the polymerization, carbonates with isolated CO$_4$-tetrahedra or carbonates with groups, rings, chains or pyramids can be formed (see the figure). The structural variety of those carbonates resembles that of silicates and some borates. In the present study, we will give an overview of carbonates containing CO$_4$-groups and present crystal-chemical aspects of CO$_4$-groups in comparison to SiO$_4$ and other MO$_4$ complex anions.

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References
Polymerization of CO4-groups

<table>
<thead>
<tr>
<th>Pyramid</th>
<th>Ring</th>
<th>Isolated</th>
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<tbody>
<tr>
<td>MnC2O2.Fd3m (Charlton et al. 2020)</td>
<td>Fe22.6Mg0.76C2O3-C2/m (Bouard et al. 2015)</td>
<td>Fe6C3O12-R3c (Cerantola et al. 2017)</td>
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<tr>
<td>CaC2O2-i42d (Konig et al. 2022)</td>
<td>Ca7.8Fe2.8Mg0.8C2O3-Pnma (Merlini et al. 2017)</td>
<td>Ca3CO3-Pnma (Larie et al. 2020; Binck et al. 2020; Spahr et al. 2021)</td>
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<td>Mg2C2O2-C2/m (Oganov et al. 2008; Bouard et al. 2011; Maedo et al. 2017; Binck et al. 2020)</td>
<td>Fe6Mg2.6C2O3-C2/m (Charlton et al. 2020)</td>
<td>Sr2[CO3]O4-I4/mcm</td>
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<tr>
<td>Sr2[CO3]O4-Pnma (Spahr et al. 2021)</td>
<td>Mg3C2O2-C2/m (Oganov et al. 2008; Ono et al. 2007)</td>
<td>Sr3[CO3]O-Pnma</td>
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