Structural diversity of carbonates containing CO_4 groups.

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The building blocks of 'conventional' carbonates such as calcite or magnesite are trigonal planar $[CO_3]^{2-}$-groups. These carbonates remain stable 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 [1-3]. The experimental difficulties to achieve such extreme conditions hindered an extensive investigation of $[CO_4]$-groups. In contrast to $[CO_4]$, other orthoanions $[MO_4]$ have been extensively investigated in the past. $[SiO_4]^{4-}$-tetrahedra are main building blocks in silicates and play a major role in crystallography/mineralogy. In addition to the $[SiO_4]^{4-}$-tetrahedra in silicates, further anions such as $[PO_4]^{3-}$ (phosphates), $[BO_4]^{5-}$ (borates), $[NO_4]^{3-}$ (nitrates) or $[SO_4]^{2-}$ (sulfates) are key-components in basic chemistry and are well-known building blocks of various minerals [4].

Recently, we demonstrated the synthesis of carbonates containing $[CO_4]$-groups at moderately high pressures (20-30 GPa) by reacting carbonates with oxides or CO_2 [1-3]. These carbonates have different chemical compositions than the well-known 'conventional' carbonates ($MeCO_3$) and are enriched either with the metal oxide or with CO_2 [1-3]. Some of them can even be recovered to ambient conditions [1,2]. This allowed us to investigate different structural aspects in great detail.

An interesting feature of the sp^3-carbonates is that the $[CO_4]$-groups may polymerize by corner-sharing. As a result, carbonates with isolated $[CO_4]$-tetrahedra or carbonates with groups, rings, chains or pyramids can be formed (Fig. 1).

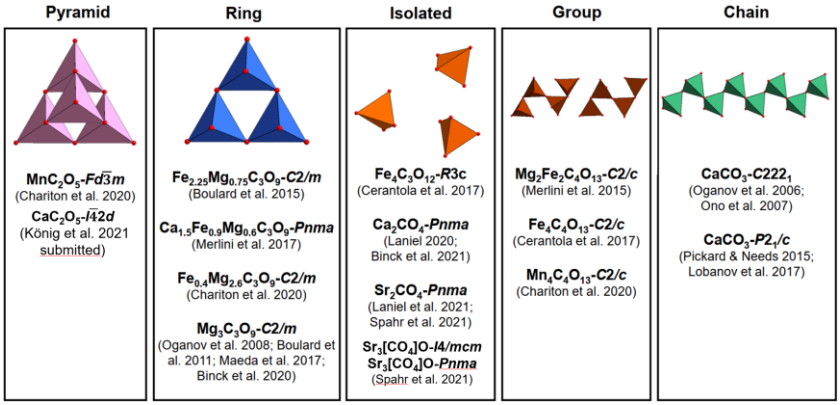

Figure 1 Structural variety of carbonates containing $[CO_4]$-tetrahedra. Further detailed references can be found in [1].

The structural variety is reminiscent of the structural variability of silicates [5]. In the study presented here we will give an overview of carbonates containing $[CO_4]$-groups and will present crystal-chemical aspects of $[CO_4]$-groups in comparison to $[SiO_4]$ and other $[MO_4]$ complex anions.

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