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The system Na₂O-CaO-SiO₂: 90 years of research, but do we really know everything?

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In their landmark paper from 1925 Morey & Bowen [1] presented the first comprehensive description of the phase relationships and melting behavior of the compounds belonging to the ternary system Na₂O-CaO-SiO₂. Due to its fundamental importance for many fields of industrial inorganic chemistry and technical mineralogy this system has been in the focus of a large number of subsequent studies dealing with both basic and applied aspects of silicate science. After more than 90 years of research activities one should assume that no problems remain to be solved.

In the course of an ongoing project on the high-temperature chemistry of compounds in the systems M₂O-RO-SiO₂ (M: Na, K; R: Ca, Sr, Ba) we realized that even for the most intensively studied Na-Ca-silicates suspicion has to be attached not only to what concerns their melting characteristics but also to what concerns the number of existing phases. Despite the compounds whose existence has been unequivocally proofed by a combination of chemical analysis and crystal structure determination there is still a large number of phases mentioned in the literature which, at best, have been characterized by unindexed powder diffraction patterns. Furthermore, in many cases even the compositions have not been thoroughly studied after synthesis. This information, however, is definitely of great importance when dealing with volatile components such as Na₂O or K₂O at temperatures above 1000°C.

We were able to demonstrate that Na₂Ca₆Si₄O₁₅, for example, which has been first synthesized via hydrothermal methods [2] can be also obtained under dry conditions using Na₂CO₃, CaCO₃ and SiO₂ as educts. Therefore, the ternary phase diagram, where this compound has not been taken into consideration, has to be revised. In-situ high-temperature powder diffraction experiments were used to determine the thermal expansion tensor of Na₂Ca₆Si₄O₁₅ between ambient temperature and 1100°C. Furthermore, the crystal structure of a new high-temperature polymorph of the compound has been determined. Finally, comprehensive synthesis experiments using solid state reactions as well as re-crystallization studies from glasses revealed that several previously described sodium calcium silicates such as Na₈Ca₃Si₅O₁₇, Na₂Ca₃Si₂O₈ and Na₂CaSi₅O₁₂ could not be reproduced indicating that a question mark has to be put on their existence.

References:

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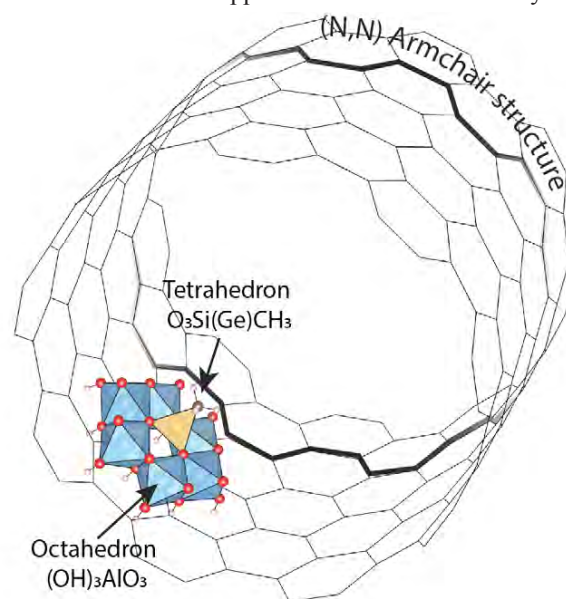
Structural resolution of inorganic nanotubes with complex stoichiometry

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Determination of the atomic structure of inorganic single-walled nanotubes with complex stoichiometry remains elusive due to the too many atomic coordinates to be fitted with respect to X-ray diffractograms inherently exhibiting rather broad features. Here we introduce a new approach which enables resolution of their structure [1]. It is based, first, on the use of helical symmetries allowing one to consider the smallest unit cell and then on semi-empirical energy minimization leading to a reduction of the number of structural parameters to be fitted. We applied this method to recently synthesized methylated alumino-silicate and alumino-germanate imogolite nanotubes of nominal composition (OH)₃Al₂O₃Si(Ge)CH₃ [2]. Imogolite (OH)₃Al₂O₃Si(OH) is a clay mineral present in soils, also synthesized by soft chemistry. Thanks to their chemical versatility, imogolite-like nanotubes (INT) are promising candidates for applications in molecular storage, recognition and separation [3]. Fit of wide-angle X-ray scattering (WAXS) diagrams of methylated INTs enabled us to determine their atomic structure. We show that unlike their (N,0) zigzag hydroxylated analogs (OH)₃Al₂O₃Si(Ge)OH, methylated imogolite nanotubes roll up into a (N,N) armchair structure. (Figure). The transferability of the approach opens up for improved understanding of structure-property relationships of inorganic nanotubes, including minerals nanotubes, to the benefit of fundamental and applicative research in these systems.



References:

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[3] D.-Y. Kang et al. (2014). *Nat Commun*, 5, 3342.

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