

FA2-MS02-O1

Be Smart: Let Minerals Inspire You to Find Exciting Materials. Wulf Depmeier. *Institute of Geosciences, University of Kiel, Kiel, Germany.*
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Rocks and minerals have most probably been used as materials ever since the earliest days of mankind. Early usages were certainly restricted to as-found, or at most primitively processed species, but soon industrial processes, like ore smelting or sintering, extended the application fields of representatives of the mineral kingdom. Roughly at the middle of the past century a revolution occurred, as more and more tailor-made materials were asked for, having specific properties or functionalities, both being defined by the requirements of modern civilization: materials sciences emerged calling for materials with compositions or devices with scales, shapes or architecture never seen in Nature before. From this development one could easily come to the conclusion that for our present needs and with respect to materials sciences Nature does not have much to offer. However, we believe that such a conclusion would at least be rather premature, and we want to check out to what extent the contrary might be true.

While it cannot be denied that Nature has its limitations – e.g. it is most probable that one will never find a naturally occurring mineral species containing just one rare earth element, or a multilayer of thin films doped correctly for a specific purpose - there are cases where we still can get inspiration, or even advice, from Nature. The examples discussed in this contribution will comprise boracites, hetero-polyhedral microporous materials, nano-sized structures and bio-inorganics, some of which referring to the proceedings of a recent relevant workshop [1].

[1] Krivovichev, S. V. (Ed.) *Minerals as Advanced Materials I*. Berlin, Heidelberg: Springer, 2008, 255 p.

Keywords: nature-inspired; minerals; materials

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Rhodesite-type Structure: A Source of Microporous Materials. Giovanni Ferraris^a, Marcella Cadoni^a. ^a*Università di Torino - Dpt. Scienze Mineralogiche e Petrologiche and NIS Centre of Excellence-Torino, Italy.*

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Minerals and synthetic phases belonging to the rhodesite mero-pleisotype series are modular microporous hydrous silicate phases based on a heteropolyhedral framework [1]. The structure is based on a double silicate layer that is formed via corner sharing of two apophyllite-like tetrahedral sheets and alternates with different types of “octahedral” layer; Na, K, Ca, Ba, Sr and REE are typical “octahedral” cations. The silicate layer is crossed by eight-membered channels along two different directions that, in rhodesite and other members, have quite circular section showing an effective channel width (ecw) of about 3 Å. The rhodesite series is merotypic because the silicate module

alternates with a variable octahedral layer; it is plesiotypic because the ratio between the numbers of up- and down-pointing tetrahedra in the apophyllite-like sheets may vary. The rhodesite-type microporous structure shows at the same time layered and heteropolyhedral-framework features. The former aspect allows synthesizing chemically different compounds while keeping constant a layer of the structure. Contrary to the porous materials whose framework is based only on tetrahedra (e.g., zeolites), which can be occupied by a limited number of cations, the heteropolyhedral frameworks allow a wider chemical variability, because the higher coordination polyhedra (e.g., octahedra) can host a large variety of cations. The heteropolyhedral porous structures are well represented in the mineral realm [2] and often were the incentive for the synthesis of new compounds suitable for technological applications [e.g., ion exchange and luminescence due to the presence of rare earth elements (REE) in the framework]. Several synthetic members of the rhodesite series have been described; here we present four new members of the rhodesite series that were obtained, by hydrothermal synthesis using 25-ml Teflon-lined stainless-steel autoclaves, as part of our research programme aiming at the synthesis of microporous silicates. For short, the four new members are named TR03, TR04, TR09 and TR10. The octahedral cations are NaKCa and NaKSr in TR03 and TR04, in the order; both TR09 and TR10 contain NaSr only. In TR03 and TR09 the octahedral layer consists of a row of octahedra alternated by a row of isolated octahedra; in TR04 and TR10 all the octahedral sites are occupied. TR09 and TR10 are unique among the about fifteen members of the series because the channels are strongly ellipsoidal such that ecw is not larger than 2 Å in one direction. Besides the common interest of these compounds as microporous materials, TR03 and TR04 have a mineralogical interest because they can be usefully compared to hydrodelhayelite and to delhayelite.

[1] Ferraris, G., Makovicky, E., Merlino, S. *Crystallography of modular materials*. IUCr/Oxford Univ. Press 2008. [2] Ferraris, G., Merlino, S. (Eds.) *Micro and mesoporous mineral phases*. Mineral. Soc. America 2005.

Keywords: microporous structure; rhodesite-type structure; hydrothermal synthesis

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Crystalline Textures in Silica-Carbonates Biomorphs. Juan Manuel García-Ruiz. *Laboratorio de Estudios Cristalográficos. Factoria Española de Cristalización. Granada, España.*

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Silica-carbonate biomorphs are nanocrystalline self-assembled materials made by purely inorganic processes, which display shapes that –like those produced by living organisms- are not controlled by crystallographic symmetry [1]. These morphologies are highly reminiscent of the shape of primitive organisms, but the precipitate are clearly inorganic in origin and form without involvement of biological compounds or living organisms [2]. The synthesis requires only a source of carbonate ions (e.g. atmospheric

CO₂), strong alkaline aqueous solutions, silica and alkaline-earth cations (Ba and Sr, Ca) at room temperature. Under these alkaline conditions, the precipitation of alkaline-earth carbonates (witherrite, strontianite or calcite/aragonite) coupled with silica precipitation entering an autocatalytic mechanism that explains their bizarre morphological behaviour, hierarchy and self-organization [3]. In this communication, rather than on morphology I will focus on the description and explanation of the crystalline texture of silica biomorphs and their relevance to the understanding of the formation of biomineral structures.

[1] *Geology* 26, 1998, 843. [2] *Science* 302, 2003, 1194. [3] *Science* 323, 2009, 362.

Keywords: crystallization; self-assembled textures; biomorphs

FA2-MS02-O4

Electronic and Magnetic Structure of Pyroxenes I: Hedenbergite, CaFeSi₂O₆. Michael Grodzicki^a, Günther Redhammer^a, Michael Reissner^b, Walter Steiner^b, Georg Amthauer^a. ^a*Department of Materials Engineering and Physics, Salzburg University, Austria.* ^b*TU Vienna, Austria.*

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The electronic and magnetic structure of the chain silicate hedenbergite (CaFe²⁺Si₂O₆) has been investigated by a number of experimental methods (neutron diffraction, Mössbauer spectroscopy, low temperature magnetic measurements), as well as by electronic structure calculations for clusters of different size in the local spin density approximation. The calculated size-converged spectroscopic data (*d-d* excitation energies, hyperfine parameters) are in quantitative agreement with the respective experimental values. The calculated magnetic coupling constants are about +25 cm⁻¹ and -4 cm⁻¹ for intra-chain and inter-chain coupling, respectively. The latter value shows that weak superexchange via edges of silicon tetrahedra is well reproduced by the calculations, and it is in qualitative agreement with an observed metamagnetic transition at 4.2 K in an external magnetic field with an onset around 4 T but saturation is not achieved in fields up to 14.5 T. The large ferromagnetic intra-chain coupling is attributed to a nearly degenerate ground state. The ratio between the two magnetic coupling constants agrees with earlier estimates on similar compounds. Finally, it is demonstrated how the detailed discussion of the various exchange pathways contributes to an improved understanding of the connection between magnetic properties and the geometrical structure.

Keywords: hedenbergite; mössbauer spectroscopy; magnetic measurements

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Structural Characterization of Maya Blue Analogous Hybrid Pigments. Catherine Dejoie^a, Pauline Martinetto^a, Eric Dooryhée^a, Devendro

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The search for stable dyes, resisting heat and moisture in particular, places several organic-inorganic hybrids as particularly appropriate and environmentally friendly solutions: the colour can be durably fixed by trapping or encapsulating the organic dye on a mineral or in a clay matrix [1]. In the present work, we examine the diffusion and the fixing process of the indigo molecules inside the cages and channels of appropriate alumino-silicates such as zeolites. We succeed in producing a stable composite, whose colour and stability resemble those of the historical Maya Blue pigment [2]. Part of our project is to revisit the structural and spectroscopic features of Maya Blue using the indigo-zeolite complex as a model case. Our new zeolitic analogues are characterized by optical and vibrational spectroscopies, quasi-elastic neutron scattering, and synchrotron X-ray powder diffraction. Formation of the hybrid is followed by in situ X-ray diffraction. Insertion of the indigo molecules inside the matrix causes a monoclinic-to-orthorhombic structural change of the zeolite crystal. Fourier difference syntheses reveal extra electronic density inside the zeolitic channels due to the presence of the organic dye. The global organic molecule position in the channel network of the zeolite is obtained by simulated annealing. Further structure refinements complete the structural determination of this new organic-inorganic hybrid.

[1] Gomez-Romero P., Sanchez C., *New J. Chem.*, 29, 2005. [2] Gettens R.J. *American Antiquity*, 7, 1962.

Keywords: rietveld refinement; zeolite; structure solution