

**MS41 P01**

**Crystal chemistry and magnetic properties of  $\text{Cu}_5\text{FeS}_4$  (bornite): a Mössbauer study.** M. Borgheresi<sup>a</sup>, F. Di Benedetto<sup>a</sup>, M. Romanelli<sup>b</sup>, G.P. Bernardini<sup>a</sup>, W. Lottermoser<sup>c</sup>, G. Tippelt<sup>c</sup>, G. Amthauer<sup>c</sup>, <sup>a</sup>*Department of Earth Sciences and Natural History Museum, University of Florence, Italy.* <sup>b</sup>*Department of Chemistry, University of Florence, Italy.* <sup>c</sup>*Department of Materials Engineering and Physics, University of Salzburg, Austria.* E-mail: [georg.amthauer@sbg.ac.at](mailto:georg.amthauer@sbg.ac.at)

**Keywords:** bornite, crystal chemistry, magnetism, Mössbauer

$\text{Cu}_5\text{FeS}_4$  (bornite) is an interesting compound because (i) it is one of the most important ore minerals for copper and (ii) it has special semiconducting and magnetic properties used in several high-tech materials, e.g. diluted magnetic semiconductors. Bornite occurs in three different polymorphs, i.e. high bornite (Fm3m), intermediate bornite (Fm3m), and low bornite (Pbca), connected by superstructure relationships. In high bornite, vacancies and metal-ions are completely disordered, in low bornite completely ordered.

Bornite orders antiferromagnetically at  $T_N \sim 64$  K [1, 2, 3] and undergoes additional transitions at 35(3) K and 10 K [4]. Below 64 K, bornite is a collinear antiferromagnet with spins oriented parallel and antiparallel to the b-axis [1]. Concerning the crystal chemistry of bornite, major open questions still are (i) the valence state of Fe and Cu and (ii) the nature of the magnetic phase transitions at low temperatures which are not yet really understood.

The aim of the present investigation is to perform a Mössbauer study of bornite at temperatures below RT and by this (i) to contribute to the solution of the problem of site occupancy, valence state and chemical bonding of Fe in bornite and (ii) to obtain more informations on the phase transitions in the antiferromagnetic stability field. Results of this study will be reported at the conference.

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**MS41 P02**

**Synthesis and structural studies of the ettringite group of minerals** S. Cairns, and C. Wilson, *Department of Chemistry, University of Glasgow, Glasgow*; C. A. Kirk, *Department of Mineralogy, Natural History Museum, London.*

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**Keywords:** Ettringite Hydrothermal Synthesis, Single Crystal Neutron Diffraction

Thaumasite ( $\text{Ca}_6[\text{Si}(\text{OH})_6.12\text{H}_2\text{O}]_2(\text{SO}_4)_2(\text{CO}_3)_2$ ) and ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}.26\text{H}_2\text{O}$ ) are members of the Ettringite group of minerals, with the general formula  $\text{Ca}_6\text{X}_2(\text{SO}_4)_3(\text{OH})_{12}.26\text{H}_2\text{O}$ , where X = Al, Cr, Fe, Mn, Si and the sulphate group can be substituted by carbonate or borate groups. Although the minerals are compositionally closely related, structurally they are different. Ettringite and Thaumasite<sup>1</sup> are the most important members of the

group as they form in cement pastes, mortars and concretes. They are formed by the action of sulfates on cement and concrete – the sulfate attack results in softening and disintegration of the cement matrix. This has major implications for the construction industry and further study into the structure of these compounds is required to address this issue.

The water structure and hydrogen bonding network in the Ettringite group of minerals are of particular interest, because they contain large amounts of water, approximately 40% by weight. It is clear from the importance of water structure to the integrity of these minerals that a detailed knowledge of the hydrogen positions in these structures is important to understanding the formation and stability of these minerals.

A systematic study of the structural chemistry of Ettringite, Thaumasite and their related phases is being undertaken using powder and single crystal x-ray diffraction, single crystal neutron diffraction, IR, TGA, DSC and SEM of both natural and synthetic samples<sup>2</sup>. Although structural determinations have previously been carried out for several members of the Ettringite group, no systematic study has been carried out to investigate the structural relationships between them. A detailed phase diagram exploration is one of the aims of our programme, to include analysis of synthetic analogues of these mineral phases and investigations into potential solid solutions that may exist between different members of the Ettringite group.

The initial stages of a synthesis programme have begun, designed to provide single crystals of ettringite and new analogues of the ettringite family. It is my intention to report on the progress of both our synthetic programme and structural investigations into these minerals.

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**MS41 P03**

**Influence of particle size on the thermal decomposition of calcite** George E. Christidis<sup>a</sup>, George Triantafyllou<sup>a</sup>, <sup>a</sup>*Technical University of Crete, Department of Mineral Resources Engineering, 73100 Chania, Greece.* E-mail: [christid@mred.tuc.gr](mailto:christid@mred.tuc.gr)

**Keywords:** calcite, thermal decomposition, isothermal sections

Thermal decomposition of calcite has been studied thoroughly in the past due to its significance on the formation of lime. Lime and slaked lime are important synthetic industrial minerals, which are utilized in numerous industrial applications. In this study we examined the influence of crystal size on the thermal decomposition of calcite present in carbonate rocks from various places of Greece. The carbonate materials used are micritic limestones from Kefalonia (Lk) and Arta (La) areas with 18.5% and 3.2% porosity respectively and 4.1  $\mu\text{m}$  and 1.5  $\mu\text{m}$  mean grain size respectively, and marbles from Asfendou, Crete (Ma) and Naxos Island (Mn) each with 4% porosity and 335  $\mu\text{m}$  and 656  $\mu\text{m}$  mean grain size respectively [1]. The kinetics of thermal decomposition of calcite in the various materials was tested with Time-Temperature-Transformation (TTT) diagrams and isothermal curves obtained from TG analysis. The onset of the conversion of calcite to lime occurs at 640°C for all

carbonate materials. The reaction begins faster in Lk compared to the other carbonate rocks. For all materials the decomposition was completed at 900°C. For Lk completion of decomposition is observed after 1½ hour, whereas for the remaining samples the reaction is completed after 2 hours.

The isothermal curves were obtained in the temperature range 640-900°C. The time required achieving maximum decomposition decreased with temperature and the isothermal curves converge at higher temperatures. Moreover the shape of isothermal curves changed from almost linear at 640°C and 700°C to sigmoid at higher temperatures. Lk is the most reactive material, because decomposition proceeds faster, whereas Mn is the least reactive carbonate. However the reaction rate for thermal decomposition of calcite is not controlled solely by grain size, because La with minimum calcite grain size displays isothermal curves comparable to Ma, which has considerably larger grain size (1.5 µm and 335 µm for Lk and Ma respectively). The role of porosity is also significant for the progress of decomposition reaction. The porosity of La is comparable to that of Ma and Mn. The firing properties affect lime reactivity as was shown by the specific surface area (SSA) and slaking temperature of the carbonate rocks [1].

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#### MS41 P04

**Transmission electron microscopy studies on a tetrasilic mica** V.K. Kis<sup>a</sup>, I. Dódony<sup>b</sup>, J-L. Robert<sup>c</sup>

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**Keywords:** mica; crystal structure; electron microscopy

Tetrasilic magnesium mica crystals synthesized hydrothermally (500 C°, 1 kbar) were studied using transmission electron microscopy. The aim of this work is to characterize the distribution of magnesium over octahedral and interlayer sites.

The size of the mica crystals varies in the 200 nm and 2 µm range. Energy filtered [001] selected area electron diffraction (SAED) patterns around 0.8 Å resolutions were recorded and quantitatively evaluated. The thickness of the platelets, estimated from the SAED resolutions, varies between 60-90 Å, i.e. 6-9 mica layers. This small thickness value allows using kinematical approximation. Two types of SAED patterns were obtained: compared to the calculated SAED patterns of phlogopite the abundant ones show unusual intensity distribution with strong  $h = 2n$  reflections on the  $k = 6n$  rows, however crystals with phlogopite-like intensity distributions also occur. The energy filtered [001] high resolution (HR)TEM images showing components up to 1.7 Å<sup>-1</sup> on their Fourier transform, revealed characteristic heterogeneities at nanometre scale.

The results of analytical (A)TEM revealed two groups in crystal compositions. In the case of dominant group the Mg/Si ratio is larger than the expected 0.75 value for a trioctahedral tetrasilic mica, whereas the K/Si ratio is

smaller than the expectable 0.25 value. The magnesium excess is located into the interlayer space in the deduced formula;  $(K_{0.8}Mg_{0.2})Mg_3[Si_4O_{11.2}(OH)_{0.8}]$ . By its composition the dominant phase of the sample proved to be a trioctahedral tetrasilic oxymica. No straightforward correlation between the different compositions and SAED patterns were observed.

The cation distributions over octahedral and interlayer sites are measured crystal by crystal in their [001] projected SAED patterns and corresponding HRTEM images.

#### MS41 P05

**Influence of the symmetry on the Raman spectra of isolated SbS<sub>3</sub> pyramids.** Sherif Kharbish<sup>a,b</sup>, Eugen Libowizky<sup>a</sup>, Anton Beran<sup>a</sup>. <sup>a</sup>*Institut für Mineralogie und Kristallographie, Geozentrum, Althanstraße 14, A-1090 Wien, Austria.* <sup>b</sup>*Geology Department, Faculty of Science, Zagazig University, Zagazig City, El-Sharkia, Egypt.*  
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**Keywords:** Raman spectroscopy, SbS<sub>3</sub> pyramids, vibration

The flat pyramidal four-atom SbS<sub>3</sub> group in tetrahedrite and pyrrargyrite with C<sub>3v</sub> symmetry and in stephanite and bournonite with C<sub>s</sub> symmetry has been investigated at room temperature by Raman spectroscopy. The fundamental stretching and bending vibrations of the pyramidal SbS<sub>3</sub> groups occur between 150 and 400 cm<sup>-1</sup>. In addition to a "lattice mode", four prominent peaks and shoulders occur in the spectra of tetrahedrite and pyrrargyrite, representing the symmetric and antisymmetric stretching ν<sub>1</sub> (A<sub>1</sub>) and ν<sub>3</sub> (E) and bending vibrations ν<sub>2</sub> (A<sub>1</sub>) and ν<sub>4</sub> (E). The bands at 362 and 350 cm<sup>-1</sup> in tetrahedrite and at 323 and 300 cm<sup>-1</sup> in pyrrargyrite were assigned to the ν<sub>1</sub> and ν<sub>3</sub> modes, respectively. The bands representing the ν<sub>2</sub> and ν<sub>4</sub> modes occur at 324 and 298 cm<sup>-1</sup> in tetrahedrite and at 274 and 252 cm<sup>-1</sup> in pyrrargyrite, respectively. In comparison with the spectra of tetrahedrite and pyrrargyrite, two to four additional bands occur in the spectra of stephanite and bournonite. Peak fitting of the stephanite and bournonite spectra give band maxima at 335, 319, 301, 233, 204 and 178 cm<sup>-1</sup> and at 335, 324, 293, 275, 227, 197, 168 and 110 cm<sup>-1</sup>, respectively. The increase of the number of the bands in stephanite and bournonite can be attributed to the splitting of the degenerate ν<sub>3</sub> (E) and ν<sub>4</sub> (E) modes due to lowering of the symmetry of the SbS<sub>3</sub> pyramids [1]. Comparison between the spectra of the C<sub>3v</sub> isolated pyramidal SbS<sub>3</sub> groups in tetrahedrite and pyrrargyrite and those of the C<sub>s</sub> isolated SbS<sub>3</sub> pyramids in stephanite and bournonite shows amazing similarities in the rough pattern of the spectra and the number of the strong bands. However, the band positions decrease continuously in wavenumber from tetrahedrite to bournonite, stephanite and pyrrargyrite. The similar band pattern of the investigated minerals may be attributed to the only small distortion of the SbS<sub>3</sub> pyramid in stephanite and bournonite. The shift of the positions of the bands in stephanite and bournonite to lower wavenumber regions relative to those in tetrahedrite can be attributed to the increasing Sb-S distances. The latter observation can also explain the shift of the band positions in the bournonite spectra to higher frequencies relative to those in pyrrargyrite with larger bond lengths. It has also been noticed that although the pyramidal SbS<sub>3</sub> groups in stephanite have larger bond lengths than those in