

# *EUG XI*



Theme AI

Contributions of Industrial Geosciences  
to Fundamental Understanding  
and Vice Versa



# *EUG XI*



Symposium AI01

Contributions of Industrial Geosciences  
to Fundamental Understanding  
and Vice Versa:  
Building Materials

Convenor

Bruno Messiga

## AI01 Building Materials

### Sunday PO Session

#### AI01 : SUpo01 : PO Systematic Investigation on Thermal Degradation of Marble by Thermal Dilatation Measurements

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Marbles as building stones as well as in their natural environment show complex weathering phenomena. While some marbles are relatively resistant others show a proceeded decohesion of the individual calcite and/or dolomite grains. Thermal micro cracking is supposed to be responsible for the initial stage of degradation (Siegesmund et al. 2000a). The most important damage scenario is based on the highly anisotropic thermal dilatation coefficient of calcite and dolomite. Generally, type and degree of the proneness to weathering of a marble are controlled by the rock's fabric, i.e. grain size, grain shape, lattice preferred orientation etc. (Siegesmund et al. 2000b). Therefore 17 different marbles from quarries with different fabric properties were systematically investigated. Thermal expansion measurements were performed by using a triple dilatometer using samples with a size of 10x10x50 mm. To determine the complete thermal expansion anisotropy samples in six independent directions were used. The temperature range was subdivided into three temperature ramps in order to characterize the temperature dependence of thermal degradation. The first ramp covered a temperature range from 25°C to 40°C, the second from 25°C to 60°C and the last from 25°C up to 85°C. The last ramp was measured twice in order to investigate if the degradation proceeds even if the final temperature was not exceeded. All the samples exhibit a directional dependence of the thermal expansion. Values for the relative thermal expansion vary between 0.176 mm/m to 1.157 mm/m within one sample. Some marbles show an almost linear anisotropic expansion behavior even up to the maximum temperature which can be attributed to the single-crystal constants and lattice preferred orientation (texture) of the rock-forming minerals (calcite, dolomite). The others exhibit a non-linear expansion as a result of i) a buffering by preexisting micro cracks or ii) thermally induced micro cracks resulting in a residual strain (Siegesmund et al 2000a). The amount of the residual strain depends on the maximum reached temperature in a certain sample direction. After the repeated measurement up to 85°C no significant change of the residual strain was observed. The correlation between the degree of thermal expansion and the corresponding residual strain is not unequivocal. Hence the marbles are classified in different groups (a) strong anisotropic dilatation/non residual strain, (b) strong anisotropic dilatation/weak residual strain and (c) strong anisotropic dilatation/strong residual strain (d) weak anisotropic dilatation/strong residual strain and (e) weak anisotropic dilatation/weak residual strain. Finally the measurements exhibit that the degradation of marble is depending on the rock fabric.

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Siegesmund S, Ullemeyer K, Weiss T, Tschegg EK, *Int. J Earth Sci, 89, 170-182, (2000b).*

#### AI01 : SUpo02 : PO Degradation of Marble: Diagnosis of Deterioration by Ultrasonic Velocity Measurements

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Natural building stones are extensively used for constructive and decorative matters all over the world. In particular marbles are preferred due to their light color and translucence. However, the limited durability of marble causes several problems. Bowing of facade panels and a pervasive structural disintegration are the most prominent damage

scenarios. This degradation is supposed to be caused by thermally-induced microcrack formation. The resulting crack porosity provides pathways for further physical, chemical and biological effects. There are a number of different parameters controlling thermal microcracking (Siegesmund et al., 2000). The predominant parameters are the grain size and the grain shape, i.e. the rock's fabric. The thermal expansion coefficient of calcite is very anisotropic. Since every individual single crystal contracts parallel to the crystallographic a-axis and expands parallel the c-axis with increasing temperature, thermal stresses between the grains are produced promoting propagation of thermally-induced microcracks. Magnitude and orientation of these microcracks should be closely linked to the individual grain to grain orientations and to the bulk lattice preferred orientation (texture) of calcite in a marble. We investigate a number of marbles with remarkably different fabric properties. The basic aim is to characterize intrinsic (matrix-related) and extrinsic (crack-related) anisotropy using a combination of a detailed and quantitative fabric analysis and spatially resolving ultrasonic velocity measurements. Ultrasonic velocity measurements are increasingly used as a non-destructive tool for the assessment of the rock's state-of-deterioration. Anisotropy effects have been widely neglected until present. While the intrinsic anisotropy is caused by the texture of the rock-forming minerals and their single-crystal properties, the extrinsic anisotropy is caused by natural (formed during the geological history) and artificial (caused by manufacturing and weathering) cracks or crack systems. Microcracks reduce ultrasonic wave velocities, and the magnitude of this reduction is proportional to the crack type and crack density (Weiss et al., 2000). Even the result of one thermal treatment of the specimens up to 100°C is already clearly visible by significantly reduced ultrasonic velocities. Thus, magnitude and directional dependence of thermally induced microcracks can be determined when the measurements of the naturally and artificially cracked samples are compared. The evaluations reveal that there exist a large difference between both, magnitude and directional dependence, of the intrinsic and extrinsic parameters for the different marbles, respectively. This difference can be explained when the fabric of the marbles is comprehensively characterized. The experimental observations are supported by mathematical models for the intrinsic (Siegesmund and Dahms, 1996) and extrinsic (O'Connell and Budiansky, 1974; Rasolofosaon et al., 2000) anisotropy parameters.

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Siegesmund S, Ullemeyer K, Weiss T & Tschegg EK, *Int. Journ. Earth Sciences*, **89/1**, 170-182, (2000).

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Weiss T, Siegesmund S & Rasolofosaon P, *Proc. 9th Int. Congress on deterioration and Conservation of stone*, **1**, 215-223, (2000).

#### AI01 : SUpo03 : PO Microstructural Features and the Durability of Building Stones: White Apuan Marbles

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Marbles from the Apuan Alps (NW Tuscany, Italy) have been widely used both in the ancient and modern times for architectural and other art works. Despite their homogeneous chemical and mineralogical composition, white marbles quarried in the Apuan Alps show a different behaviour when placed in external environment. This is due to the microstructural features related to the particular tectonic evolution of the Apuan Alps (Molli et al., 2000). These features greatly affect behaviour with respect to the water absorption and the fluid circulation. These parameters are closely linked to durability. Marbles with granoblastic ("foam") structures show total open porosity, saturation index and imbibition coefficients higher than those with slightly curved or embayed to sutured grain boundaries (Barsottelli et al., 1998; Cantisani et al., 2000). In this paper we investigate the relationship between the microstructures of some types of Apuan white marbles, the

petrophysical characteristics (porosity, imbibition coefficients, saturation index) and their durability. For this purpose, thermal cycles in the climatic chamber have been carried out on distinct samples, using the following cycle: - from room temperature to -10°C with a gradient of 1.00°C at minute; - at -10°C for 20 minutes; - from -10°C to +80°C with a gradient of 2.25°C at minute; - at +80°C for 20 minutes. This cycle was repeated 300 times and at pre-established time intervals, the variation in the petrophysical parameters of the samples was determined. The petrophysical analysis of artificial ageing samples has confirmed that marbles with granoblastic structures are more affected by thermal shocks. Trends concerning total open porosity and qualitative and quantitative variation in mesoporosity have been related to marbles with different microstructures. The intergranular micro cracks in different types of marbles have been quantitatively evaluated by image analysis. The artificial aged samples have been compared with naturally aged marbles in the Florence Cathedral.

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Cantisani E., Canova R., Fratini F., Manganelli Del Fa C. & Molli G., *Periodico di mineralogia*, (2000).

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#### AI01 : SUpo04 : PO Survey on Historic Building Materials: Contributions to a Regional Conservation Concept

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A study concerned with building materials of monuments in South Tyrol (Italy) has been conducted in the frame of an Italian-Austrian EU-Interreg-II program. The aim of the project was twofold: (1) documentation of the material inventory of churches and (2) investigation of the properties and weathering behaviour of the main building materials. The first part of the study, presented here, involves mapping on a regional scale to survey the distribution of historic building materials, mainly of churches. Due to the complex construction of many buildings, geological mapping has to consider the different material demands within a building, based on the architectural considerations. This is somewhat relieved by the fact that in most cases only a limited number of different stone materials was used for a single building. To present all informations on a map in the known topographical sign for churches the geological information was inscribed. Based on the architectural features a division into 4 different categories including i) general architectural elements; ii) base; iii) walls; and iv) tower was performed. A further subdivision to consider two materials in one category is also possible. This scheme presents these data very clear with a maximum of information about the building materials as well as their preferred use in different parts of the building. Therefore it summarises the geological data for conservational needs. The preliminary results of the mapping survey indicate a close correlation of the building materials of the historic buildings with the local geology except for specific architectural stone elements. In the alpine region of South Tyrol all different types of rocks exposed in the area were used. Furthermore it was possible to identify different building materials in specific architectural positions, which reflects the influence of physical properties such as hardness and cleavage etc. In addition, a correlation to the historic quarries still needs to be done. The aim of this study was to make geological knowledge about building materials and their sources available to art historians as well as conservers and to contribute to conservation practice on a regional scale.

## AI01 Building Materials

AI01 : SUpo05 : PO

### Raw Materials of the Neolithic/Aeneolithic Polished Stone Artefacts: Their Migration Paths in Europe (IGCP/UNESCO Project No. 442)

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Though several individuals as well as working teams in various European countries have been involved in the petroarchaeological/archaeometrical problematic, the IGCP/UNESCO Nr. 442 project, is the first broadly formulated international project in this (archaeology/geosciences) field. The will of both scientific communities, i. e. archaeologists and geoscientists from 24 countries close collaborate, project leader regards as the most distinguished achievement in the frame of the IGCP programme. The most topical goal of the project, characterization of raw material used by the Neolithic populations and to follow traces of raw material (implements) communication paths in Europe, via expected results will positively influence knowledge of mentioned aspects in the frame of the world cultural heritage. Objects of study: Neolithic archaeological artefacts (tools, weapons etc.) Method of study: laboratory, methods used in geosciences (thin section, X-ray diffraction, microprobe, DTA studies, chemical composition: main, trace as well as REE determination ao.) Main goals of the project: (a) contribution for better understanding of material culture of the Neolithic/Aeneolithic populations, (b) to gather and to sum up all available information on raw material types used by the Neolithic/Aeneolithic populations for stone implements construction, (c) to join discrete raw material types with known geological bodies, (d) to define (to present on the map) communication paths of raw materials/ready made tools, weapons etc. on the European continent. Results: heritage of mankind (world heritage). List of meetings. Realization of Inaugural meeting of the IGCP/UNESCO Project r. 442 (June 21st, 1999, Bratislava, Slovak Republic). 20 participants from 8 countries - Austria, Czech Republic, Hungary, Poland, U.S.A., Spain, Italy, Slovak Republic. 1st workshop (Bratislava, Slovak Republic) and excursion to the Natural History Museum in Wien, (June 22nd-23rd, 1999, Wien - Austria). 2nd workshop (October 11th-13th 1999, Veszprém, Hungary) applied around 60 participants from 8 countries - Hungary, Czech Republic, Austria, Slovak Republic, Poland, Croatia, Israel, Italy. 3rd workshop (September 27-29, 2000, Eggenburg, Austria) has been attended by 28 participants of the project from 6 countries (Czech Republic, Hungary, Austria, Poland, Austria, Slovak Republic) to present and discuss new results on Neolithic/Aeneolithic raw material types studied on the territory of various countries by individuals or teams of researchers Selected publications. In KRYSTALINIKUM 26 (Contribution to the Geology and Petrology of crystalline complexes, Brno 2000, Czech Republic) are 14 publications with problematics of the Neolithic/Aeneolithic polished stone tools from Italy, Croatia, Ireland, Czech Republic, Spain, Poland, Slovak Republic, Yugoslavia and Hungary. Others selected publications are in references.

Presented abstract represents partial result of the IGCP/UNESCO Project No 442.

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Farkas Z & Hovorka D, *Materialia Archaeologica Slovaca, tomus II*, 75-80, (1999).

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Starnini E & Szakmány Gy, *Acta Arch. Acad. Sci. Hungaricae*, **50**, 98, 279-342, (2000).

AI01 : SUpo06 : PO

### High-Pressure Metabasites: Peculiar Raw Materials of Neolithic/Aeneolithic Populations of Central Europe

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In the frame of the IGCP/UNESCO Project No 442 authors gathered basic information on raw material types used by Neolithic/Aeneolithic populations (Hovorka and Illá\_ová, 2000) in central Europe. Peculiar type of raw materials, from the territory of Slovakia, is represented by rocks being product of high pressure metamorphic processes. Simplectic eclogite hammer-axe has been described from site Nitriansky Hrádok (35 km s. of town Nitra: Hovorka et al. 1996). Eclogite bears typical features of retrogressive recrystallization. They are characteristic for eclogites of the Bohemian Massif, but not for the Eastern Alps. Eclogites are not known in the Western Carpathians mountain system. Based on small size of discussed implement we suppose transport of eclogite pebble from the eastern rim of the Bohemian Massif by river Morava and Danube. Distance of the site of find from the Danube river is 30 km. Eclogite as a raw material for implement construction is unusual also from the point of view of its relatively coarse grain-size (round 3 mm) pattern. In the very last time in the implements collection found on site Svod'n (excavations by Nimcová-Pavúková 1971-1983) we have described (Spisiak and Hovorka, in print) small flat non bored axe made from very fine grained almandine-omphacite eclogite. Characteristic are atoll garnets (16-21 Prp and 68-70% Alm) in some places of rectangular morphology and transition to "full" garnet crystals. Omphacite (Morimoto et al. 1988) belongs to two subtypes based on its Ca, Mg and Al contents. For the given rock characteristic is seldom presence of idioblastic (to 2 mm) anorthite (95% An) crystals filled up by very fine grained products of its recrystallization. Eclogites with atoll garnets are known from the Mariánske Lázne complex (Bohemian Massif): in this case presence of kyanite and not anorthite is reported. We consider long distance transport (from the Western Alps ?) of the given implement. Third peculiar raw material type is represented by monomineralic jadeite, which from axe found on site Senica (western Slovakia) has been elaborated (Hovorka et al. 1998). Microprobe analyses of jadeite (of gradually diminishing Na contents) allow to reconstruct geological "history" of given raw material type. In the central Europe small jadeite bodies occur only in Eastern Sudetes (sw. Poland). So also in this case long distance transport (from the Western Alps ?) ought to be taken into consideration. Mentioned high pressure rock types represent peculiar raw material occurring along with prevailing greenschists, amphibolites, antigorite serpentinites, alkali basalts and the other "common" raw material types. Presented abstract represents partial result of the IGCP/UNESCO Project No 442.

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AI01 : SUpo07 : PO

### Experimental Investigation of Kaolinite and Illite-Bearing Clays: Microtextures and Reaction Progress

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In ceramics chemical and mineral composition of raw material strongly influence the fabric and the mineral assemblage produced by firing. When temperature increases reactions between temper minerals and clay matrix occur along grain boundaries and this constrains typology and composition of firing phases (Maggetti, 1986; Riccardi and Messiga, 1999).

The aim of this work is to describe the microtexture evolution and the changes of mineral assemblages occurring during temperature increasing. Experiments have been undertaken on two clayey mixtures respectively composed of illite and kaolinite; calcite and quartz fragments (about 20%, in volume) have been added to both. Ten experimental samples have been fired in a furnace under oxidising conditions, at 500°, 700°, 800°, 900° and 1050°C. Results obtained by experimental runs, carried out using diffusion couples (see Capasso et al., this volume), have been used for comparison. Analyses and microtexture investigations were performed on polished, C-coated thin sections. Analytical data produced with 'in situ' techniques (EMP) are combined with powder X-ray diffraction (XRD). Particular attention has been paid on illite-calcite, illite-quartz, kaolinite-calcite, kaolinite-quartz reactions.

In the illite clay, calcite breaks down at 500°C, giving CaO+CO<sub>2</sub>; at 800°C illite reacts with CaO producing gehlenite; at 1050°C quartz reacts with illite giving anorthite. In the kaolinite clay at 800°C calcite reacts with kaolinite giving gehlenite. No reactions occur between kaolin and quartz, even at 1050°C. Diffusion experiments indicate that kaolin-lime pair firstly react at 1200°C and produces anorthite as firing phase. At 1300°C, gehlenite and wollastonite together with anorthite appear.

A comparison of reaction path-ways in both investigated systems indicates that the illite-bearing system is more reactive than the kaolinite-bearing. In the kaolinite-lime system the firing phases forming-reactions occur at higher temperatures than in the calcite-kaolin-quartz system. This can be accounted to the catalytic effect exerted by the CO<sub>2</sub> fluid phase released by calcite break-down.

Maggetti M, *Fortschr. Miner.*, **64**, 1, 87-103, (1986).

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AI01 : SUpo08 : PO

### Utilization of Zircon Sands in Ceramic Industry

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Zircon is the most used opacifier for ceramic glazes. A relevant aspect in the use of zircon as an opacifier is related to its physical and chemical properties, such as particle size distribution and composition (trace elements, inclusions, rare-earth diffusion...), that are involved in the comminution and preparation of glazes. In particular the Van De Hulst formula (Van De Hulst, 1957), correlating the mean diameter of the zircon sand particles with the refractive index of both the opacifier and glass, points to the optimization of the production procedure. An accurate and exhaustive characterization of the raw material represented by the zircon sands is, therefore, a necessary prerequisite for any further application. Seven zircon sands of different beach placers, provided by the Colorobbia Group, (Italy), have been investigated for their chemical, mineralogical and morphological characteristics. While the morphometric characteristics have been established using both grain size distribution and automatic image analysis, the morphotropic ones have been elaborated directly from their images. The chemical composition has been detected using XRF, ICP-AES, and INAA for the rare earths. Mineralogical composition has been established by optical and XRD investigation, while a Raman microprobe has been used for the characterization of the inclusions. The grain size image analysis gives two populations with different mean values and different box plots amplitudes, while the morphotropic analysis does not show any difference for all sands, thus suggesting the use of similar separation and zircon-enrichment procedures for the raw material beneficiation. As to their chemical composition in particular the distribution of Ca, Na and Eu ppm contents evidences the presence of two groups corresponding to the provenance of the sands, i. e. South Africa and Australia. On the other hand the distribution of the U-content is strictly correlated with the automatic image grain size distribution, thus confirming the influence of the metamictization process on the mechanical properties. Rutile inclusions were found in all investigated sands, while fluid

## AI01 Building Materials

inclusion could not be identified because the extremely small size of the grains prevented to obtain suitable thin sections.

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### AI01 : SUpo09 : PO Synthesis of Na-A Zeolite from Halloysite 10 Å

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Total synthesis of Na-A zeolite has been obtained by the use of natural Halloysite 10Å, found near Grosseto (Italy), instead of the expensive chemical products, Na aluminates and Na silicates, currently used in industry. Na-A zeolite is largely used by detergent industry. In this field it substitutes Na-tripoliphosphate (NTP) which is considered one of the main responsible of the eutrophication of superficial water. High concentrations of pure halloysite have been found inside vugs, lenses and geods present in metalliferous mineralization (Fe, Mn sulphides) outcropping near Grosseto (Central Italy). Chemical analysis of halloysite points out the absence of rutile and scarcity of zircon. This suggests a genesis connected to seafloor precipitation from acid solutions inside pre-existent vugs (Di Sabatino et al., 1996). We experimentally studied the limits of stability of Halloysite 10Å and Halloysite 7Å in dry and wet conditions. In dry conditions, at 303°K the transformation of Halloysite 10Å in Halloysite 7Å occurs in six days, meanwhile in wet conditions, at 330°K, the same phase changing is completed after three days. In order to transform Halloysite 10Å in Na-A zeolite, we made a set of experiences at different temperatures (318°, 340° and 353°K), putting Halloysite 10Å in an alkaline solution (NaOH, 2.5 M). The kinetic of destruction-reaction of Halloysite is controlled through periodical sampling and XRD analysis. Experiences were stopped as we obtained total transformation in Hydroxysodalite (HS). At 318°K Halloysite 10Å reacts rapidly and transform itself in Halloysite 7Å only partially; this transformation is, in fact, lower in time than the crystallisation of "Na-A" and "Na-G" zeolites. As transformation proceeds HS totally substitutes with time both Halloysite and Na-A and Na-G zeolites. At 318° K total and isolated crystallisation of Na-A zeolite is impossible because of the phase overlapping (Halloysite, Na-A, Na-G and HS). Lattice destruction of Halloysite 10Å, at 340°K, in presence of water happens more and more rapidly. Also in this case we don't reach 100 per cent in crystallisation of isolated pure Na-A zeolite. This is due to the overlapping of Na-G zeolite and to the beginning of HS nucleation. At 353°K disappearance of Halloysite happens more rapidly; we eliminate the formation of Na-G zeolite and reach the total crystallisation of Na-A zeolite. Crystallisation times are drastically reduced (1 hour and 30 minutes) at these temperatures and are comparable with the industrial ones.

### AI01 : SUpo10 : PO Synthesis of Na-A and Na-X Zeolites from Tripolaceous Deposits

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Within the neogenic deposits that filled Crotona Basin (Calabria, Southern Italy) are present tripolaceous levels messinian in age. "Tripoli" are porous and friable rocks made of thin white and grey layers. They often preserve macroscopic remains of marine fossils. They are biogenic deposits whose genesis is due to the accumulation of siliceous organisms (radiolarians, diatoms, and sponges); these fix silica, naturally dissolved in the marine water, with biochemical mechanisms. Tripoli deposits represent a considerable resource between siliceous rocks. Their industrial use is concerned with construction of strong explosives; they also are used as abrasives in detergents. Tripoli mineral assemblage is made of quartz, amorphous opaline silica, montmorillonite, chlorite, kaolinite, k-micas, calcite and carbonates. Our work aims to a new industrial exploitation of the material attained by the synthesis of zeolitic minerals. Zeolites are hydrated aluminosilicates of alkaline and earthy-alkaline elements. Both the ion exchange and the selective adsorption properties of zeolites are at the base of several industrial uses. These are based on the capabilities

of certain zeolites to exchange cations selectively from aqueous solutions. Some uses deal with radioactive-waste water treatment, sewage effluent treatment, agricultural-waste waters treatment. One method of zeolitic synthesis refers to the use of reagents like alkaline aluminates (Na<sub>2</sub>Al<sub>2</sub>O<sub>7</sub>) and alkaline silicates (Na<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>). Chemical treatments have been made on tripolaceous samples in order to obtain the Na<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>. Tripoli has first been attached by HCl to eliminate the calcite and carbonate fraction and Fe and Mn oxides. The same sample was then immersed in an alkaline solution (NaOH, 3 M) so to induce the solubilization of the fossil fraction and the precipitation of an insoluble fraction (quartz and clay minerals). The solution Na<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>·nH<sub>2</sub>O made of amorphous opaline silica has then been combined with NaAlO<sub>2</sub> to obtain the Na-A and Na-X zeolitic phases.

### AI01 : SUpo11 : PO Replacement in Concrete of Cement for Slurry from the Processing of Aggregates from Basaltic Rocks: Assessment of Replacement Feasibility Through Concrete Rupture Modulus Determination

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In the islands of the Madeira archipelago, there is not cement production, due to the non existence of any deposits of the traditional raw materials needed for cement manufacture, such as: limestone, clay, sand and gypsum. The annual importation of cement is estimated at 550,000 tonnes.

All islands of the Madeira archipelago are of volcanic nature, consisting mainly of basalt, trachybasalt, trachyte and lapilli tuff of trachytic composition. There are several quarries where harder rock types are fragmented to produce aggregates of distinct grain size. Fragmentation yields fine stone dust and when aggregates are washed slurries or muds are produced which are conducted to decantation tanks, taken out, dried and disposed nearby. No use has been found so far for these slurries or muds.

Experiments were carried out through which concrete of C25 type (concrete that stands the load of 25 Mpa) was prepared, from initial mixtures of 50 liters consisting of coarse aggregate (three size grades), fine aggregate (sand from the sea), cement, dry mud and water. In these mixtures cement/water ratio was equal to 1, on a weight basis. Four compositions were prepared in which 5%, 10%, 15%, and 20% of the cement total content was replaced, by equal percentages of dry mud, on a weight basis. From each of the mixtures referred to series of three cubes with dimensions 15 cm x 15 cm x 15 cm were prepared and the mean values of their rupture modulus were determined after setting or maturing for 3, 7 and 28 days. The replacement of 15% of cement for mud imparts higher resistance to flexion comparatively to the initial formulation.

Another set of experiments was carried out replacing in the concrete formulation, the component fine sand by mud. Four compositions were prepared in which 20%, 40%, 60% and 80% of sand was replaced by equal percentages of dry mud, on a weight basis. The replacement of 20% of fine aggregate (sand) for mud do not change the mechanical resistance to flexion of the concrete.

Therefore, important financial savings and environmental benefits could be achieved in case of mud being incorporated in concrete formulations at the optimum levels referred to.

Mud fine grain size and its chemical composition (high Si, Ca, Fe, Mg and Na contents) are considered as being the major factors which favour the pozzolanic behaviour.

### AI01 : SUpo12 : PO Investigations of the Mineralogic/Chemical Reactions in Roadways of Salt Mines Based on Crushed Salt Rock and Water

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Roadways in mines have to withstand the high stresses caused by the driving of large numbers of heavy vehicles. In salt mines, they are made by spreading pre-crushed salt rock on the base of the underground excavations, compacting it and moistening it with water. A detailed description of the method gave Grübler (1968).

The moistening with water improves the compaction process of the grains. However it causes a dissolution of evaporite minerals of the crushed rock salt and to a lesser extent of the rocks at the base and walls of the underground excavations. The fluids react, besides halite, with varying amounts of anhydrite (CaSO<sub>4</sub>), polyhalite (Ca<sub>2</sub>K<sub>2</sub>Mg(SO<sub>4</sub>)<sub>6</sub>·2H<sub>2</sub>O), and in some cases with carnallite (KMgCl<sub>3</sub>·6H<sub>2</sub>O). Due to the polyhalite content of the rock salt develop saline solution which are saturated with regard to calcium sulfate minerals, such as anhydrite and glauberite (Na<sub>2</sub>Ca(SO<sub>4</sub>)<sub>2</sub>). In the case of a higher potassium concentration the solutions are saturated by syngenite (K<sub>2</sub>Ca(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O). However, under normal circumstances a saturation of polyhalite cannot be reached, because sufficient amounts of polyhalite are not available in the rock salts.

The sodium chloride dominated brines, having water activities of more than 0.7, evaporate as a result of the low humidity in the salt mines. During this process their composition exhibits an evaporation-dependent evolution trend. However, the concentrations of the dissolved ions are modified by the precipitation of changing mineral associations. Thus, at the first stage halite crystallizes besides small amounts of Ca-sulfates. This process causes the cementation of the salt grains. During the evaporation process the pore volume of the crushed salt rock, the water activity and consequently the evaporation rate of the fluids progressively decreases. The free space between the rock salt matrix increases, because the crystals have much lower volumes in relation to the mother liquids.

The mineralogic/chemical processes can be explained on the basis of solid-liquid phase equilibria of the hexary system of oceanic salts (Na-K-Ca-Mg-Cl-SO<sub>4</sub>). The concentration of dissolved trace elements, such as bromine, make it possible to calculate the stadium of evaporation and thus enable conclusions on the kinetics of dissolution and precipitation reactions.

The in-situ investigations were compared with thermodynamic calculations by the geochemical programme EQ3/6. The examinations showed that NaCl-brines are more suitable for the construction of roadways than natural occurring magnesium chloride-rich rock solutions. They have much lower water activities (vapor pressures) and does not significantly evaporate under the conditions in salt mines. Besides the findings concerning the construction of roadways this contribution summarizes differences between natural formation waters and fluids of anthropogenic origin.

Grübler, G, *Kali u. Steinsalz*, 5, 20-26, (1968).

### AI01 : SUpo13 : PO The Interrelationship of the Mining-Induced Earthquake and Rock Burst Energies and the Consequences of these Events in the Mines

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The increase in mining scale and depth entails the increase both in number of mining-induced earthquakes and their unit power in mines. There are some examples of the most powerful events occurred recently: Solvay potassium mine, Germany, March 13, 1989, M5.5; Werra trona mine, the USA, February 5, 1995, M5.3; Umbozero rare earth mine, Russia, August 17, 1999, M4.4 and some others. Mining-induced earthquakes, whose epicentres are located just in the mining workings, are called tectonic rock bursts or disastrous rock bursts.

## AI01 Building Materials

### Monday AM Session

#### AI01 : MOam01 : G5 Natural Building Stones: Fabric Induced Anisotropy and its Influence on Mechanical Properties

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Every natural building stone represents an anisotropic and heterogeneous system. Degree and type of a fabric anisotropy may vary and is characterized by grain shape preferred orientations, microcrack systems and preferred orientations of the rock-forming minerals (here referred to as texture) etc. Consequently, the result is an anisotropy of different mechanical and physical properties (c.f. Siegesmund 1996). In order to characterize the relationship between fabric anisotropy and directional dependence of physical properties a series of increasingly deformed mylonites from the Sesia-Lanzo-Zone (northern Italy) (c.f. Techmer 1996) and three commercially used gneisses were analyzed. Most prominent anisotropy-bearing minerals in gneisses are mica, which possess a high single-crystal anisotropy. A progressive degree of deformation coincides with increasingly aligned mica which form the macroscopically visible foliation. A lineation is characterized by a preferred alignment of elongated quartz and feldspar grains. To constrain type and degree the fabric anisotropy the textures of the rock forming minerals were measured by neutron diffraction and with a universal-stage at an optical microscope. Information on orientations of microcrack systems can be obtained by the measurement of ultrasonic compressional wave velocities on spherical samples under various confining pressures (Rasolofosaon et al. 1999). The fabric-induced anisotropy of mechanical properties was determined by compressive, bending and indirect tensile strength tests. Mechanical tests were performed by considering a minimum of three mutually perpendicular sample orientations. In general the mechanical properties of the Sesia-Lanzo mylonites and the gneisses are strongly related to rock fabric. Bending strength, indirect tensile strength and compressive strength vary in dependence on the orientation of mica cleavage cracks. A maximum compressive strength is observed perpendicular to them, whereas for bending and tensile strength the opposite effect is valid. An additional influencing parameter is the grain shape anisotropy of the other rock-forming minerals quartz and feldspar. A prolate fabric causes higher strength values parallel to the longer axis whereas in the case of oblate fabric the strength values according to the mica cleavage cracks (parallel to foliation) are similar. However, some of the analyzed rocks with an oblate fabric exhibit a different behavior, since the tensile strength varies in the two mutually perpendicular directions within the foliation plane. This effect is supposedly attributed to the orientation of microcrack systems.

The degree of a fabric induced anisotropy of mechanical behavior can easily reach the factor 1:2 or even more. The directional dependence of mechanical strength should be considered as a normal property of a natural building stone and detailed fabric investigations can give important information about type and degree of mechanical anisotropies.

Siegesmund S, *Geotekt. Forsch.*, **85**, 1-123, (1996).  
Techmer KS, *Z. geol. Wiss.*, **24** (5/6), 699-713, (1996).  
Rasolofosaon PNJ, Rabbel W, Siegesmund S & Vollbrecht A, *Geophys. J. Int.*, **141**, 413-424, (2000).

#### AI01 : MOam02 : G5 Control of Marble Disintegration by Fabric Properties and Thermal Dilatation

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Marbles are extensively used as natural building stones for decorative and constructive matters. However, especially in recent times they are subjected to reinforced deterioration. The initial weathering stage of marbles is characterized by crack growth due to thermal dilatation processes (Siegesmund et al., 2000). Different marbles types with remarkably different fabrics have been investigated in order

to get information about the fabric dependence of marble disintegration by thermal expansion. Therefore the results of detailed fabric analyses and thermal dilatation measurements of the respective marbles were correlated. Since the thermal expansion coefficient  $\alpha$  of calcite is extremely anisotropic  $\alpha_{11} = 26 \times 10^{-6}$  1/K parallel and  $\alpha_{22} = \alpha_{33} = -6 \times 10^{-6}$  1/K perpendicular to the crystallographic c-axis, the calcite single crystal contracts normal to the c-axis and expands parallel to the c-axis during heating. This leads to thermally induced stresses resulting in a thermal microcracking (Tschegg et al., 1999). All investigated marbles show a more or less pronounced anisotropy of thermal dilatation. This directional dependence is clearly controlled by the lattice preferred orientation of calcite (texture). A directional dependence of thermal dilatation has not necessarily to be expected perpendicular to macroscopic fabric elements like foliation, since some marbles show girdle distribution of the c-axes or c-axis maxima oblique to the foliation. The values for the thermal dilatation coefficient vary from  $2 \times 10^{-6}$  1/K to  $22 \times 10^{-6}$  1/K for the investigated marble types. At lower temperature intervals the thermal dilatation can be buffered by existing microcrack systems. Above a certain temperature the texture-based part of thermal dilatation is superposed by a permanent length-change due to thermal cracking which results in a residual strain of the sample. This residual strain also shows a directional dependence which coincides with the texture. It is higher parallel to the c-axes maximum and smaller in the direction of preferred orientation of the a-axes. Even marble from the same provenance can show different degrees of residual strain which can be traced back to fabric properties. The grain boundary geometry, which represents the final stage of a complex geological history, controls significantly the weathering behavior of a marble. Marbles with straight or only slightly curved grain boundaries are much less resistant against thermal treatment than those with strongly curved, interlocking grain boundaries. Besides the grain boundary geometry the grain size might be of importance. Marbles with larger grain sizes show thermal cracking at significantly lower temperatures. Thus, microfabric investigations in combination with thermal dilatation measurements enable a prediction of the proneness to thermal weathering of marbles.

Siegesmund S, Weiss T & Tschegg EK, *Proceedings 9th International congress on deterioration and conservation of stone*, **1**, 205-214, (2000).  
Tschegg EK, Widhalm C & Eppensteiner W, *Z. dt. geol. Ges.*, **150**, 283-297, (1999).

#### AI01 : MOam03 : G5 Frost Action on two Types of Sandstone Used in Alsation Monument Building

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Alsation monuments are built with two types of Buntsandstein sandstone : - a thin and rich type in clay mineral Meules sandstone with 23,5% of total porosity ; - a coarser and less rich type in clay mineral Vosgien sandstone with 18% of total porosity. Their porosity structure differences (homogeneity, mercury threshold, permeability...) give them mixed petrophysical properties. In particular, capillary transfer kinetics are more important in the Meules sandstone ( $A = 1,26 \text{ g/cm}^2/\text{h}^{1/2}$  ;  $B = 8,43 \text{ cm/h}^{1/2}$ ) than in the Vosgien sandstone ( $A = 0,18 \text{ g/cm}^2/\text{h}^{1/2}$  ;  $B = 1,59 \text{ cm/h}^{1/2}$ ) whereas drying kinetics are less important in the Meules sandstone (-0.008 g/cm<sup>2</sup> at 33% R.H.) than in the Vosgien sandstone (-0.016 g/cm<sup>2</sup> at 33% R.H.). 7 x 7 x 7 cm<sup>3</sup> sample series of each sandstone are isolated in waterproof sheath to maintain constant saturation during experiments : 48h partial saturation or vacuum total saturation. Samples are submitted to 24h freeze-thaw cycles which go from +12°C to -6°C. After each series, samples are dried and capillary absorption is measured. After 3 series of 30 cycles, no partial saturation tested sandstone presents macroscopic modification and total porosity values remain unchanged. On the other hand, from the first cycles, total saturation tested sandstone is fractured with increase of porosity. Cracking is important and accompanied with loss of matter on the Vosgien sandstone, while it is weaker, occurs later and without loss of matter on the Meules sandstone. Furthermore, frost decreases capillary transfer kinetics of the Vosgien sandstone whereas it has no influence on those of the Meules sandstone. This behaviour is explained by porosity structure modifications revealed by Scanning Electronic Microscope observations and mercury injection porosimetry measures on frozen or not frozen samples. However, these results are in opposition to ground observations where frost damage is exceptional on the

## AI01 Building Materials

Vosgien sandstone and often on the Meules sandstone. That comes from the experimental frost conditions where samples are maintained at partial or total constant saturation. On the building, the saturation is always partial and drying is possible. These experiments allow to bring to the fore the initial transfer properties part of rocks and the importance of saturation variations by absorption-drying cycles on frost damage.

Thomas W.N., *Building Research*, 17, (1958).  
REMY J.M., *Thèse INPL*, (1993).  
Gueguen JM, *Rapport interne ENSAIS*, (1984).

### AI01 : MOam04 : G5 Calcite Crystals as Mortar Aggregate in Northern Italy

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The use of calcitic aggregate in mortars is widespread in Northern Italy since Roman times. The availability of calcitic material is due to the presence of large calcareous outcrops in the whole Italian Southern Alps, so the river sands have a great fraction made by calcitic clasts. The use of calcite as mortar aggregate is suggested by Vitruvius mainly for rendering or decoration (De architectura book 7, chap. 3 and 6). Some mortars coming from roman buildings (1st - 2nd century AD) and others from Renaissance, Baroque and Rococo buildings (15th-18th century), were analysed in order to distinguish the raw material used in the aggregate. Two different types of analysis were performed: X-ray diffraction, optical microscopy on thin section. Sampling involved many lombard towns as Brescia, Como, Lodi, Mantova, Milano, Pavia and ancient roman towns of Bedriacum, Desenzano, Sirmio. The Roman mortars are plasters used to support wall paintings; the modern mortars are used for cornices, friezes or other decorations and as finishing coat on modelled figures. Mortars show at least two layers. The first layer (on the wall) is made by lime and quartz sand aggregate, the second one is made by lime and/or "plaster of Paris" together with calcitic aggregate (calcareous sand or artificially made aggregate). In this study we focus primarily on the aggregate artificially made by crushing limestone, marble, etc. A lot of samples show rounded polycrystalline clasts of calcite (maximum dimension of crystals in the clasts about 2 mm) or angular single crystals with perfect rhombohedral cleavage (maximum dimension about 5 mm). In the first case, the raw material is mainly marble and a comparison was carried out to see if there were differences between the features of these marble fragments and the features of different types of Italian marble: this comparison confirms this provenance. In the second case, the raw material used to make calcite crystals is not a marble: in fact the size of these crystals is incompatible with the grain size of the marbles. A comparison was carried out on a great number of calcite bearing rocks in order to identify the provenance of these crystals (calcite veins in micritic limestones, calcite veins in marbles and breccias, calcitic alabaster, calcareous concretion). The observations indicate that calcite crystals of veins have the same microscopic features of the calcite crystals used as mortar aggregates. Calcite veins are diffused also in many marbles used as building stone. So samples from Greek marble quarries of Skiros, Lésvos and Hios islands were examined and it would be possible that the calcite veins were by-product of the quarry work. The veins were crushed and the crystals were traded as mortar aggregates.

### AI01 : MOam05 : G5 Thin Section Analysis of Ancient Plaster and Mortar

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Original plasters and mortars from cultural heritage monuments are analysed to determine the composition of the building materials and to adjust the composition so that they will be more resistant in the future, e.g. against weathering. Generally, chemical analyses are carried out to characterize these ancient materials. Thus the results are interpreted in terms of the original composition of the mixture. The method contains some inaccuracies, e.g. if the binder and aggregate of a mortar are made of the same chemical material, they cannot be distinguished by chemical analyses. Furthermore, chemical analyses give no

informations about the pore structure and weathering phenomena which have affected the plaster or mortar and which are important for conservation practices. This information can be obtained when plasters are analyzed by thin sections.

Investigations of thin sections by polarization microscope is the only method which provides informations about the distribution of pores in combination with the distribution of binder and aggregate; both can be characterized and distinguished by their optical properties. Additionally, in a thin section it is possible to study the in situ weathering phenomena which have affected the plaster or mortar. An appropriate sample preparation is required to obtain all of the above mentioned results. Prior making a thin section samples (at least 2x1x1 cm in size) have to be impregnated by coloured resin which reveals sample's pores. Furthermore, the thin sections can be examined under cathodoluminescence microscope with electron microprobe to obtain the luminescence properties of the minerals and the elemental composition, which help to determine the composition of the plaster. Additionally, very fine grained binder, which often can be observed in thin sections but not identified by polarization microscope, can be investigated by SEM with EDAX to determine the composition.

Samples were investigated from different monuments in Berlin and Brandenburg. Examples of ancient lime plaster are compared with modern plaster having hydrophobic properties. Further examples are historical gypsum plaster and mortar from Halberstadt (Harz mountains) containing different types of gypsum and anhydrite; these can not be distinguished by chemical analyses.

### AI01 : MOam06 : G5 Technical Handling and Control of the Transformation of Anhydrite to Gypsum

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On the background of the enormous availability of the anhydrous calcium sulphate (anhydrite  $\text{CaSO}_4$ ) and the increasing lack of industrial available gypsum ( $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ ) deposits, that can satisfy purity requirements for special applications, we examined the hydration behaviour of anhydrite under environmental and laboratory conditions.

The hydration of anhydrite is known as a very slow occurring process. The usually described transformation mechanism is characterized by a dissolution step of the anhydrous phase and the subsequent precipitation of gypsum.

On the basis of laboratory experiments we illuminate the reaction mechanisms by observing surface reactions and the resulting products of calcium sulphate phases in aqueous solutions. This is the key for a better technical handling and control of the phase transformation.

By variation of the physico-chemical conditions, as the amount and kind of background electrolytes, pH and other system controlling factors, such as organics, it's possible to accelerate the slowly running transformation reactions.

The mechanisms of this acceleration process are still quite unclear. In consequence, our further interest has been concentrated on this acceleration process by studying the dissolution behaviour of anhydrite and the recrystallisation of gypsum.

Batch tests have been made with pure natural anhydrite and evaluated by XRD, ESEM (environmental SEM), and elemental concentrations were determined by spectroscopy (AAS).

Thus we gain insight in the frame of conditions, which influence the acceleration process.

The transformation processes have been observed in situ by Scanning Force Microscopy (SFM) and also documented by environmental scanning electron microscopy (ESEM).

A good understanding of these acceleration mechanisms permits a better technical handling of suchlike reactions and can guide to new application of the anhydrous calcium sulphate, which still plays a minor role in industrial applications.

### AI01 : MOam09 : G5 Models and Geomechanical Properties of Dense Grain Packings

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Fractal packing and highly irregular shaped particles increase the mechanical properties of rocks and building materials. This suggests that fractal methods are good tools for modeling particle mixes with efficient properties like maximum strength and maximum surface area or minimum porosity and minimum permeability. However gradings and packings are calculated by "Euclidian" disk models and sphere models. Surprisingly even the simplest models are far more complex than they appear. The fractal "Apollonian packing model" is proposed as the most universal two-dimensional packing model. However the inhomogeneity of gradings and the irregularity of natural grain shapes and surfaces are not reflected by these models. Consequently calculations are often far from empirical observations and experimental results. A thorough quantification of packings and gradings is important for many reasons and still a matter of intense investigation and controversial discussion. This study concentrates on fractal models for densely packed non-cohesive rocks, crushed mineral assemblages, concrete and asphalt mixtures. A summary of fractal grain size distributions with linear cumulative curves on log-log plots is presented for these mixtures. It is shown that fractal two-dimensional and three-dimensional models for dense packings reflect different physical processes of material mixing or geological deposition. The results from shear-box experiments on materials with distinct grain size distributions show a remarkable increase of the mechanical strength from non-fractal to fractal mixtures. It is suggested that fractal techniques need more systematic application and correlation with results from material testing experiments in engineering geology. The purpose of future work should lead towards the computability of dense packings of angular particles in three dimensions.

### AI01 : MOam10 : G5 Characterisation of the Solvus Brownmillerite-Perovskite in the $\text{CaAl}_{0.5}\text{Fe}_{0.5}\text{O}_{2.5}$ - $\text{CaTiO}_3$ System

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It has been shown recently, by Gloter et al. (2000), that submicrometer grains of brownmillerite coexist with perovskite grains and perovskite exsolution lamellae in major calcium aluminate cements (CAC). These transmission electron microscopic (TEM) observations suggest that a solvus brownmillerite-perovskite may occur in a wide range of composition of  $\text{Ca}(\text{Al},\text{Fe},\text{Ti})$  ferrites. However, due to the lack of data concerning the phase diagram of the system  $\text{CaAl}_{0.5}\text{Fe}_{0.5}\text{O}_{2.5}$  -  $\text{CaTiO}_3$  the conditions of coexistence of such phases (composition, T,  $\text{pO}_2$ ) remain poorly known. A ferrite composition  $\text{CaAl}_{0.35}\text{Ti}_{0.15}\text{Fe}_{0.5}\text{O}_{2.575}$  was synthesised from a mixture of oxides and carbonate, melted at 1600°C and quenched in air. Pieces were then annealed in air and under reducing  $\text{pO}_2$  (around  $2 \cdot 10^{-12}$  atm.) between 1250°C and 1400°C. The samples were analysed by TEM and powder X-ray diffraction before and after annealing. All samples annealed in air contain a brownmillerite phase plus a phase with an intermediate structure between brownmillerite and perovskite comparable to the phase with a 1.86 nm unit cell observed in Al-free ferrites by Marinho & Glasser, 1984 (corresponding to TOTOO stacking of tetrahedral and octahedral layers). The brownmillerite phase shows systematically twins in planes {101}, suggesting that the crystals had a higher symmetry at high temperature (perovskite structure?). Added to this microstructure in brownmillerite we observed nanometer scale exsolution lamellae that developed in {101} planes. Such exsolutions can be identified for annealing experiments performed up to 1365°C, suggesting that the apex of the solvus is higher than 1365°C. The exsolution phenomena observed in these synthetic ferrites is comparable to the brownmillerite-perovskite exsolutions analysed in CAC clinkers. However, no occurrence of phases with intermediate structure was yet reported in such clinker. In order to understand these differences of behaviour we are currently analysing samples

## AI01 Building Materials

annealed in reducing conditions in order to check the possible effect of  $pO_2$  on the phase diagram of the Al-rich ferrites.

Gloter A, Ingrin J, Bouchet D, Scrivener K & Colliex C, *Phys. Chem. Mineral*, **27**, 504-513, (2000).  
Marinho MB & Glasser FP, *Cement Concrete Res*, **14**, 360-368, (1984).

### AI01 : MOam11 : G5 Glass Ceramic Manufacts Belonging to ZnO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> System: Study of Bulk Nucleation and Crystal Growth. Chemical Physical Characterization for Industrial Applications

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Glass-ceramic materials obtained by ZnO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system can be classified by crystalline phase that develops: willemite (Zn<sub>2</sub>SiO<sub>4</sub>), gahnite (ZnAl<sub>2</sub>O<sub>4</sub>). By suitable composition of parent glass it is possible obtain affected phase. This system was utilized to obtain transparent glass ceramics acting on nucleating agents like TiO<sub>2</sub> and ZrO<sub>2</sub> and glass modifier like MgO. In this work was studied homogeneous nucleation and crystallization of glass ceramic materials, therefore without use of nucleating agents. Nucleation occurring arbitrarily throughout the system without preferential sites for nucleous formation is termed homogeneous nucleation. Is not easy obtain this form of nucleation because initial glass must be chemically, structurally and energetically homogeneous in all its parts. The glass system ZnO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and its modifications were studied without use of nucleating agents formulating a proper chemical composition of the parent glass. Substituting ZnO with MgO a less efficiency in crystallization of the glass was observed resulting in a slight devitrification on the surface. A plate of parent glass was obtained casting the melt in a graphite mould. After cooling the sample was reheated with an appropriate heat treatment in order to obtain the crystallization of the glass. XRD and SEM techniques was used to detect the crystalline phases present and to study time-temperature effect on crystallization and phase separation of glass. Good results was obtained with glass-ceramic compositions that developed gahnite as crystalline phase and a silica rich glass as residual amorphous phase. It's supposed a crystallization process from nuclei, dispersed in the bulk of glass. These nuclei are generated by spinodal decomposition of glass phase and the wide Tyndall effect produced allows to reveal their presence. The result is a spread crystallization of gahnite in a silica rich glass matrix. The processing parameters for the fusion and the casting of the material were obtained by high temperature viscosity measures. Mechanical and chemical corrosion tests were carried out on bulk crystallized samples: abrasion test, fracture resistance and acid resistance. The first results indicate that this material could be suitable for using as building material and for special uses in chemical and aerospace industry.

### AI01 : MOam12 : G5 Chromian-Rich Phases in the System MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Cr<sub>2</sub>O<sub>3</sub> and their Relevance on Chromium Inertization in Ceramic Refractories

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Storage and inertization of industrial toxic wastes containing chromium, can be approached by reinserting such element in a number of crystalline phases forming in the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (MAS). Even though phase relationships in the system MAS are well known, few data are available on phase equilibria of the quaternary system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Cr<sub>2</sub>O<sub>3</sub> (MASC).

High temperature experiments were performed on compositions lying on the spinel, corundum and mullite primary phase fields of the system MASC, aimed to study phase relations and chromium partitioning, at temperatures from 1250°C to 1560°C. Six different bulk compositions were prepared: three of them with SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>=1:1 wt.% and three with SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>=2:3 wt.%. All compositions have Cr<sub>2</sub>O<sub>3</sub>:Al<sub>2</sub>O<sub>3</sub>=1:9 in moles. Charges were enveloped in platinum foils, heated in a vertical furnace in ambient atmos-

phere, and quenched in water. Characterization of specimens was made by electron microprobe, X-ray powder diffraction and backscattered electrons imaging.

Preliminary results on such compositions showed formation of chromium-rich crystalline phases coexisting with a substantially chromium-free glass, and rearrangement of liquidus surfaces in the MASC system compared to MAS. Mullite, cordierite, sapphirine, corundum and spinel solid solutions incorporate variable amounts of chromium, as a function of temperature and specific buffering phase assemblage.

Sapphirine was found in a variety of bulk compositions, due to its large field of stability in the subsolidus. Chromium content in synthetic sapphirine obtained in compositional sections at Cr<sub>2</sub>O<sub>3</sub>:Al<sub>2</sub>O<sub>3</sub>=1:9 is much larger than in natural crystals, up to ca. 30 wt.% Cr<sub>2</sub>O<sub>3</sub>. Element distribution between solid phases reveals that Cr/Al in sapphirine > Cr/Al spinel > Cr/Al in cordierite > Cr/Al in mullite.

In order to further investigate the role of sapphirine as a chromium-reservoir in refractory assemblages, we performed synthesis experiments at temperatures ranging from 1340°C to 1480°C, on compositions corresponding to chromian sapphirines. Selected bulk compositions assume different models of site occupancies by chromium, on the basis of the low-pressure endmember [Mg<sub>2</sub>Al<sub>4</sub>]<sup>6</sup>[Al<sub>2</sub>Si<sub>4</sub>]<sup>4</sup>O<sub>40</sub>. Results along this join are integrated with phase relationships on more silica-rich compositions in order to depict a model for Cr-storage in refractory ceramics.

### AI01 : MOam13 : G5 The Join CaO-Al<sub>2</sub>(Si<sub>2</sub>O<sub>7</sub>)(OH)<sub>2</sub> (Kaolinite): An Experimental Study between 1100-1300 °C

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We investigated within the "ceramic system" CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, the reaction path-way along the binary sub-system Kaolinite - Lime, that concern ceramics commonly used as building materials.

Experimental runs were carried out using the diffusion couples method. Natural Kaolinite and Lime were used. CaO produced by thermal decomposition of calcite (1000°C, for 14 hours) has been histostatically pressed (0.2 GPa for 6 minute). The resulting tablets were sinterized in open air at 1350°C for 14 hours. Experiments were carried out keeping in contact reactants in Al<sub>2</sub>O<sub>3</sub> rods and using horizontal furnaces. No controls has been exerted on firing atmosphere. Temperatures were 1100, 1200, 1250 and 1300°C and experimental runs lasted 3.5, 7 and 14 hours. Samples was allowed to cool overnight to room temperature; only one sample (1300°C) has been quenched.

Reaction zones have been investigated on polished samples and analysed under electron microscope (textures) and electron microprobe (compositions). Experiments show that mullite replaces Kaolinite when temperature exceeds 1000°C. Reactions rims form at 1200°C, 1250°C and 1300°C for running times of 14, 7 and 3.5 hours, respectively. Three distinct bands of Anorthite, Wollastonite and Gehlenite (proceeding from Mullite to Lime) characterise the reaction zone. The reaction rims occur with variable thickness related to temperature and timing. The width of the reaction boundary is directly correlated to temperature values at constant running time as well as to timing at constant temperature. Heuedral anorthite crystals with comb textures develop at the mullite boundary. Wollastonite and Gehlenite are commonly subhedral. The quenching experiment highlights the coexistence of anorthite and melt which strongly suggests the peritectic growth of anorthite. Microtextures and mineral compositions indicate a reaction path-way starting with a peritectic-type reaction and producing melt together with anorthite crystals. Wollastonite and gehlenite crystallised during the cooling. The layer arrangement is a consequence of a diffusion-controlled distribution of components during the reaction path-way.

### AI01 : MOam14 : G5 Incorporation in Ceramic Pastes Utilized in the Manufacture of Utilitarian and Decorative Ware of Slurries Produced during the Processing of Aggregates from Volcanic Rocks

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The volcanic nature of the islands belonging to the Madeira archipelago was not favourable to the formation of deposits of ceramic raw materials. Therefore, ceramic materials, such as: bricks, roof tiles, wall tiles and floor tiles are all imported. There is just a small plant, Antiga Olaria do Lazareto, Funchal, that produces utilitarian and decorative red colored ware made of fine tuff and red soil developed on top of lapilli tuff of trachytic composition, raw materials that after being extracted in confined sites are conveniently blended with imported kaolinitic clay. On the other hand, there are several active quarries where volcanic rocks, basalt, trachybasalt and tuff are extracted and processed in order to produce both coarse and fine aggregates used in civil construction. One of these quarries, located at Funda de Cima, belongs to Brimade-Sociedade de Britas da Madeira, S.A., and produces actually around 180,000 m<sup>3</sup>/year of aggregates. The washing up of these aggregates yield slurries or muds which after decantation and drying represent around 10% in volume of the overall weight of aggregates production. So, only this quarry where basalt, trachyte and tuff agglomerate is processed produces actually around 18,000 tonnes/year of dry mud. No uses have been found yet for these fine powders which represent environmental risks, due to their high content in heavy metals and their easy transportation through wind and runoff. Experiments were carried out in order to assess the feasibility of the incorporation of these fine materials from the quarry of Funda de Cima in the ceramic pastes prepared in Antiga Olaria do Lazareto. Mud chemistry is characterized by high contents of fluxes (Fe, Ca, Mg and Na), mud mineral composition is formed by Na-Ca feldspar, hematite, goethite, mica and smectite, and 90% of the mud grain size is less than 0.060 mm. Mud has low plasticity (Atterberg plasticity index estimated at 6%), low expansibility (estimated at 14%), low extrusion moisture estimated at 15%), low dry-green retraction at 105 %C (estimated at 3%), and low dry-fired retraction at 800 %C, 900 %C and 1,000 %C (estimated at 0.6% for 5hours of residence time at 1,000 %C) and high mechanical resistance to flexion (estimated at 60 kgf/cm<sup>2</sup> for 5 hours of residence at 900 %C and 100 Kgf/cm<sup>2</sup> for 5 hours of residence time at 1,000 %C). Mud, up to 40% in weight, could be incorporated in the ceramic paste.

