MULTI-TECHNIQUE CHARACTERIZATIONS OF MARBLE STONES FROM ELEFSIS, GREECE, AND SOAPSTONES FROM GRYTDAL, NORWAY IN ACCELERATED ACID WEATHERING STUDIES

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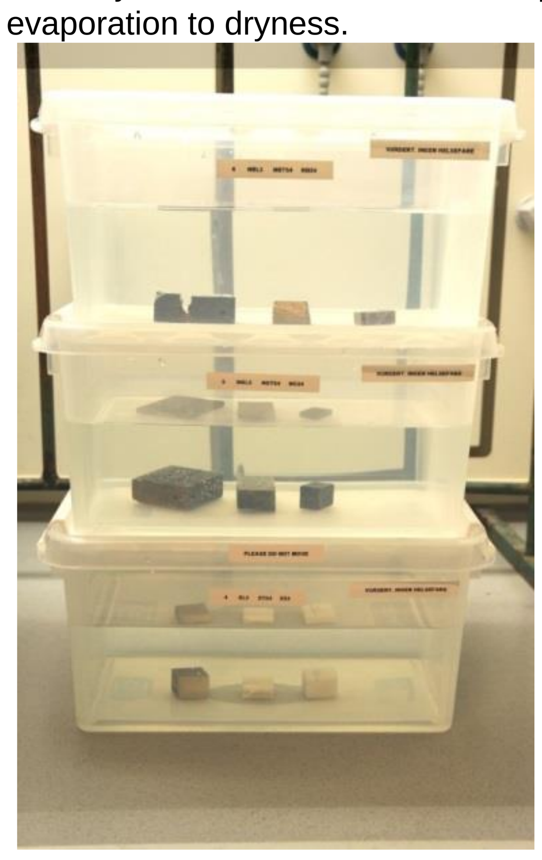
Introduction

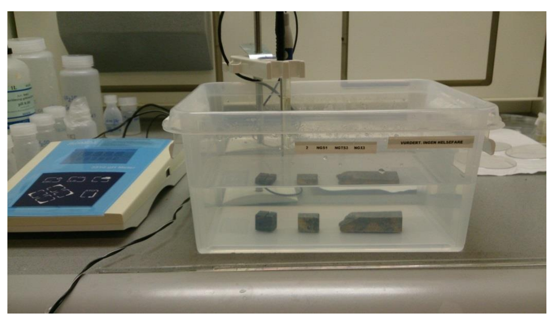
Studies on the effects of acid pollution were conducted on three types of stone samples: marble stone from Elefsis, Greece, and two types of soapstone from Grytdal, Norway. The Pentelikon marble stone from Elefsis used in columns at the archeological site in Elefsis where as the Grytdal soapstones for the construction of Nidaros Cathedral Church in Trondheim. The investigation is part of a larger project in which we attempt to estimate and predict stone erosion from weathering, in order to reconstruct earlier appearances and predict future transformations. The approach involves studies of accelerated weathering effects from salt, acid and freeze-thaw on stone samples, site exposure tests and successive high accuracy surface scanning of the monuments in which the stones have been used. For the simulation of the accelerated acid weathering two acidic conditions (nitric and sulphuric acids) at constant pH's were selected. Loss in mass with time and the physicochemical changes on macroscopic and microscopic levels were monitored, including qualitative and quantitative estimates of the acid rain-induced surface recession. The stones were analyzed before and after exposure to the acidic conditions with a range of analytical techniques. The acidic solutions used in the acid weathering simulation were evaporated to dryness and the residue investigated to identify salts produced in order to shed additional light on the deterioration processes.

Acid weathering setup

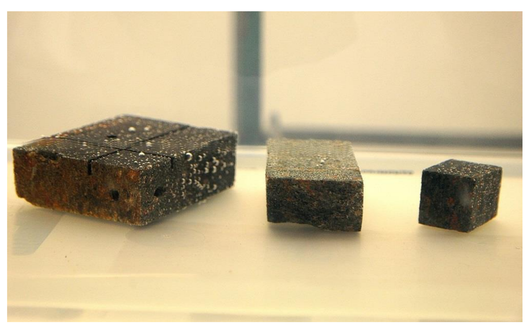
A set of three samples each from Elefsis, less weathered Grytdal and weathered stones to be used in different analyses (QEMSCAN, SEM, 3D Microscopy, XRD, and thin section preparations) were immersed in simulated acid rain solutions of sulphuric acid and a mixture of 1/3 nitric and 2/3 sulfuric acids. A total of 18 specimens were used. The pH was regularly monitored and adjusted to 4. This is to simulate the effect of SO2 and the combination of SO2 and NO2 in a wet condition. To minimize evaporation the immersion chamber comprised of a plastic box was covered. After a duration of about 10 days the stones were extracted from the solutions, dried in oven at 105 °C and their masses measured following cooling in a desiccator. The cycles continued for a month time in two rounds whereby characterization with multiple techniques were conducted. The leachates were also investigated after evaporation to dryness.



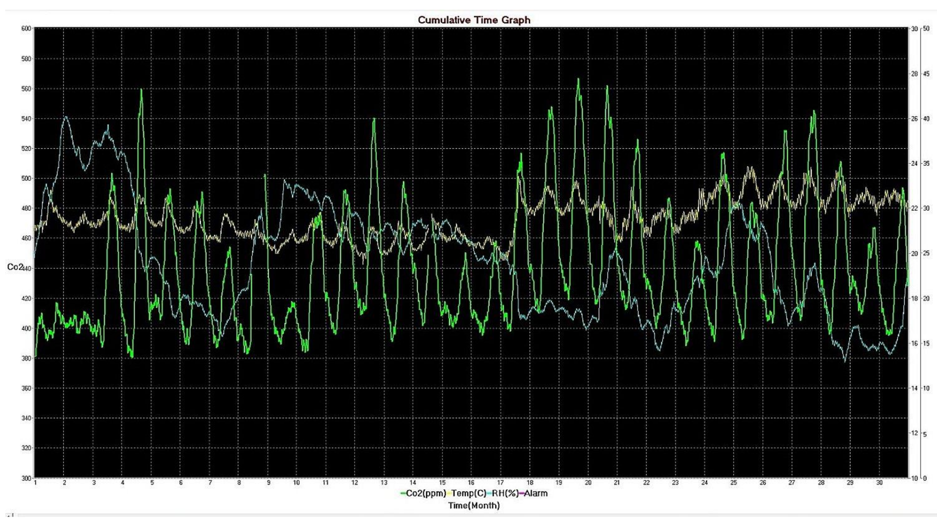
During immersion of the three sets of samples stones in separate acidic solutions



During pH monitoring and adjustment



Non-weathered Grytdal stones when in acidic solution after oven drying. Evolution of gas is noticeable. More enhanced in the weathered one..



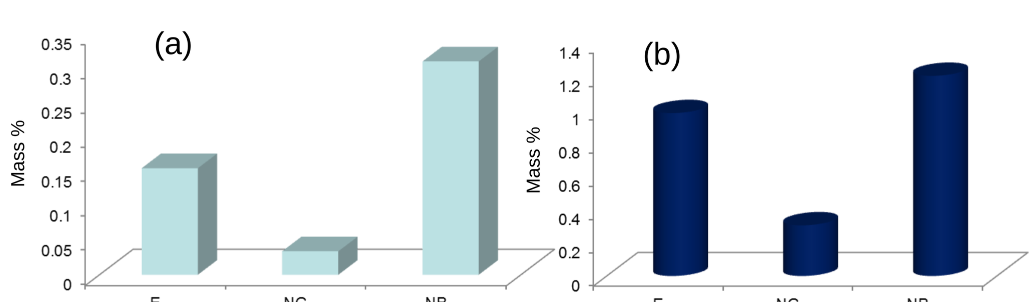
The variation in Temperature , RH and CO_2 level in November 2014 in the lab where the acid weathering was carried out.

Characterization techniques

Physicochemical characterizations before and after accelerated weathering through the use of multiple analytical and imaging techniques:

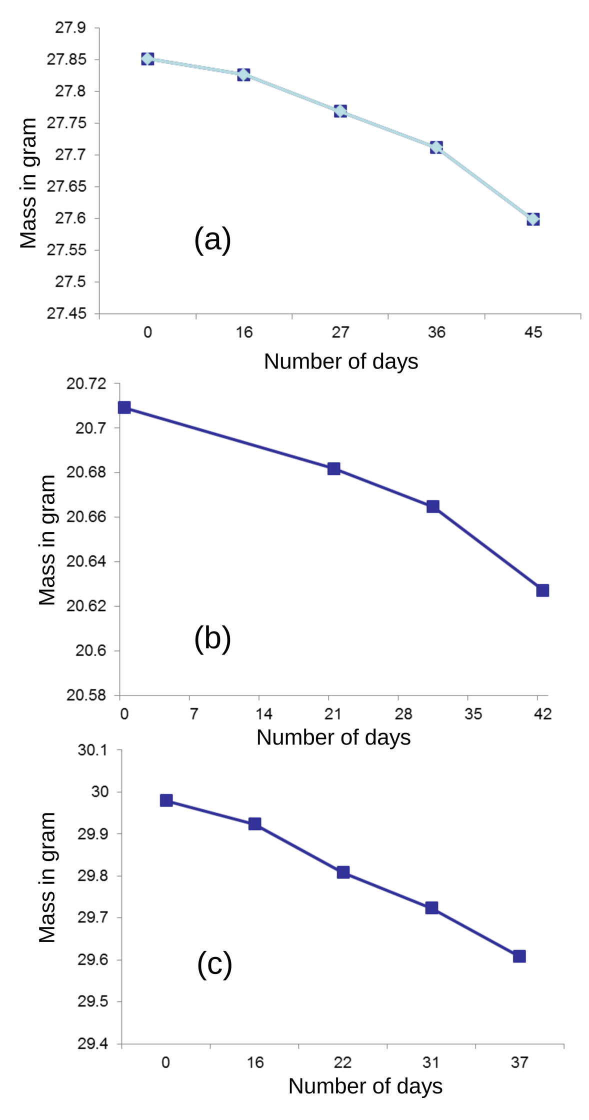
Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN), 3D Microscopy, Scanning Electron Microscope and Energy Dispersive X-Ray Spectrometry (SEM-EDX), High precision optical 3D scanning using Breukmann 3D scanner, Micro Computed Tomography (Micro-CT), X-Ray Diffraction (XRD) and Petrography, Fourier Transform Infrared spectroscopy (FTIR).

Highlights of some of the results

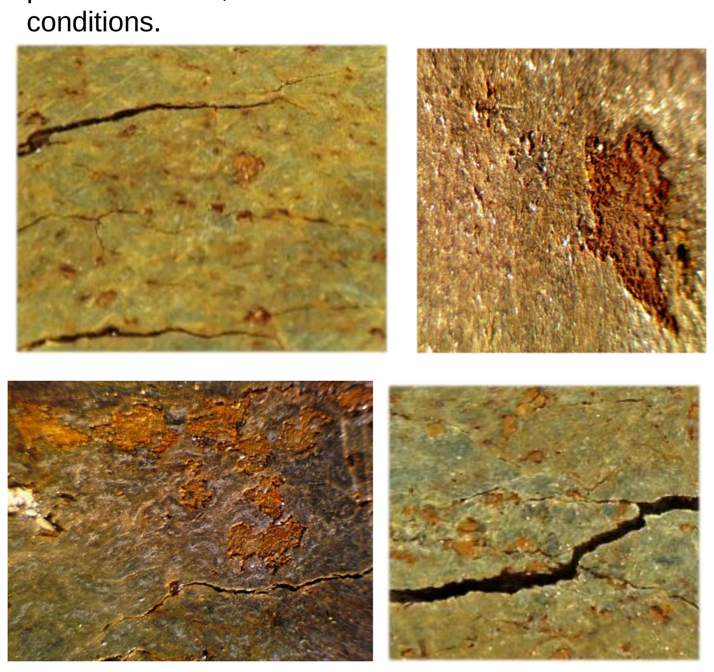


NG – Soapstone not weathered NB- Already weathered soapstone E- Marble

(a) Average percentage change in mass of the three types of stones observed after the second acid weathering round using a mixture of sulphuric and nitric acid solutions (b) using sulphuric acid. NB with more porous texture, fissures and cracks is affected the most in both conditions.

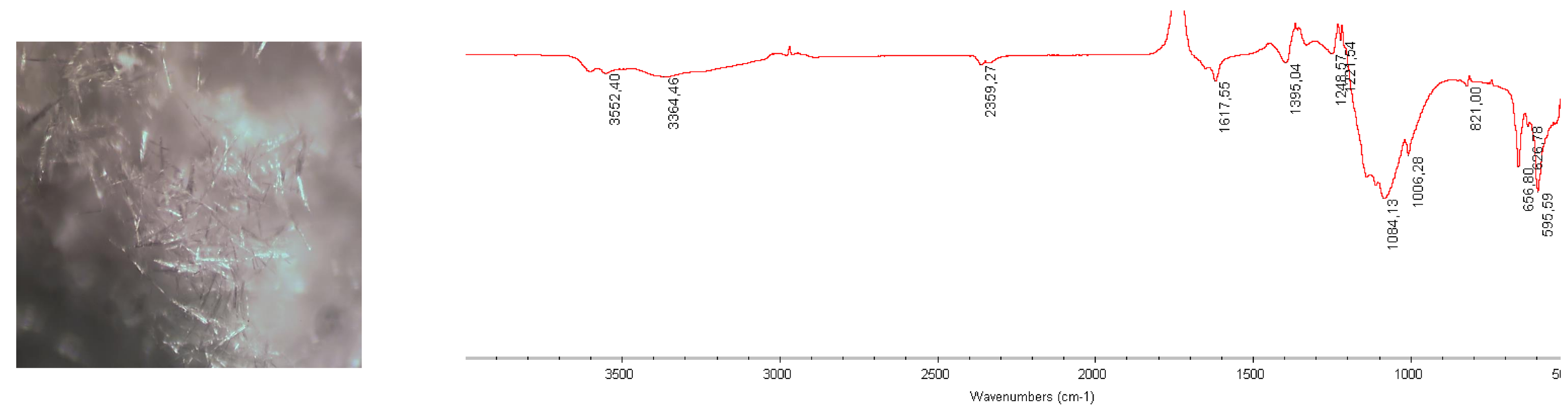


The change in mass in gram for E (a) NG (b) and NB (c) stone samples versus number of days in the first round.

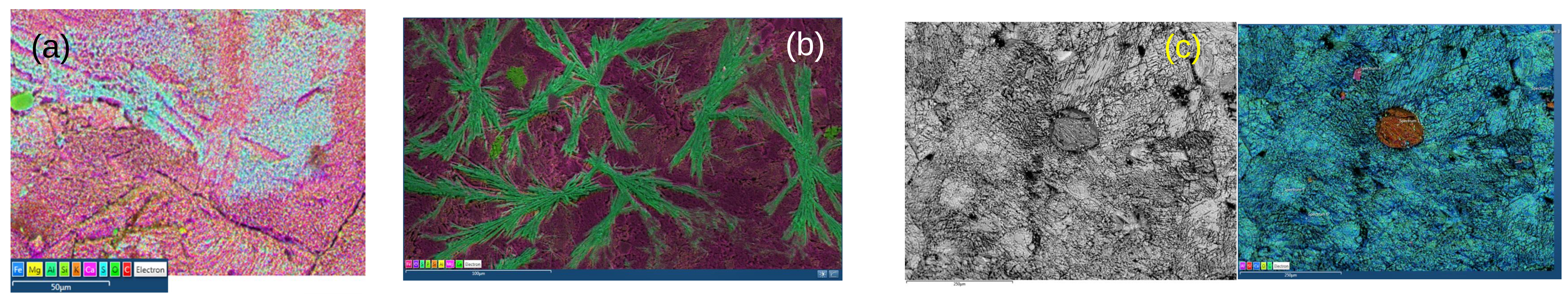


(a) Close up images of NB stones in acid mixtures in the first round with increasing cracking and enhanced eroding of iron sulfide, dolomite and iron oxide rich site (b) Iron oxide rich localities emerging and eroding faster than other parts in NB stone in sulphuric acid solution. They got yellowish\orangish in colour. The cracking gets enhanced leading to volume expansion and eventually detachment. The white precipitations are gypsum confined to selected localities.
(c) NB stones in a mixed acid solution disintegrating, flacking and cracking along layers in the second round. The porosity of the stone in terms of the number, type, size of the pores as well as fissures and cracks matter. The most porous of the three samples NB was much more seriously. An increase in volume was also noted despite high loss in mass.
(d) Formation of yellowish red spots on NG stones in sulphuric acid solution

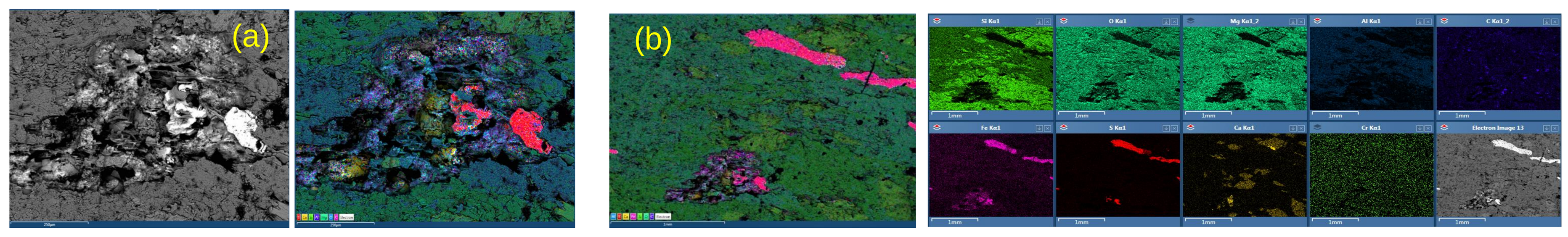
Some of the results continued



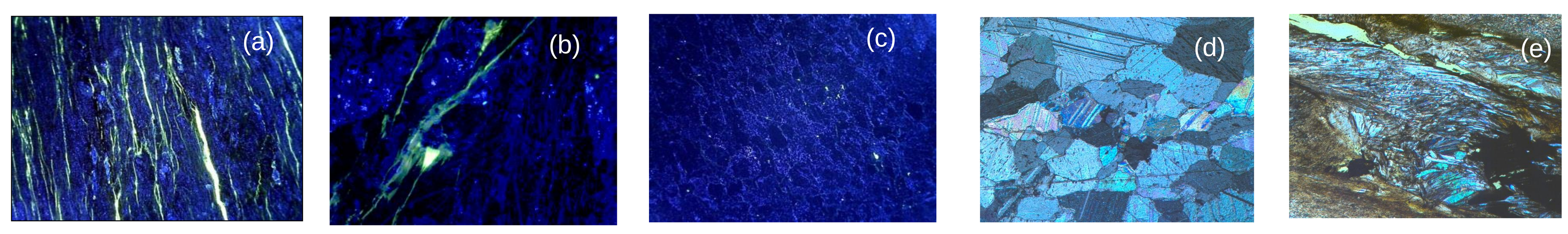
Microscopic image of the crystals formed up on drying of the leachate from sulphic solution in which Elefsis marble stones were immersed. The cyrstals are identified as gypsum from their IR spectra (a). The spectrum of gypsum from the acid mixture chamber containing NB stones (b).



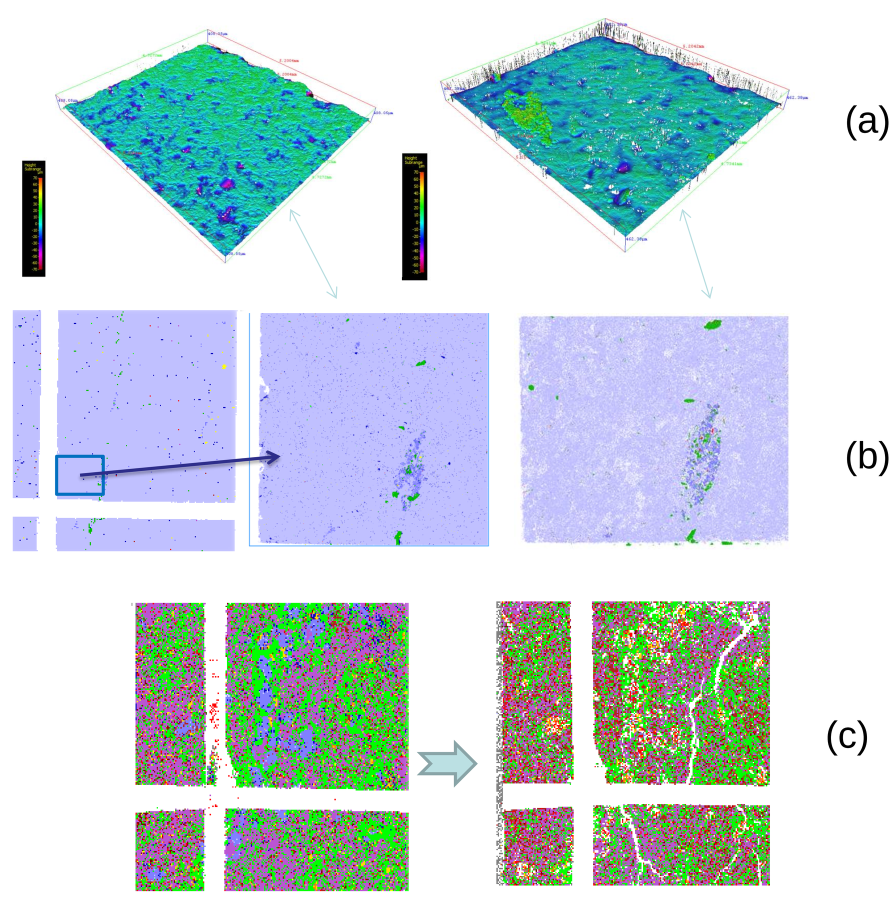
Layered elemental mapping of the surface of E in sulphuric acid solution showing the gypsum on the calcite after the second round (a). The dominant mechanism seems formation of gypsum and subsequent dissolution leading to weight loss. Layered mapping of the surface of NB stone in sulphuric acid solution after the first round (b). The deposition of gypsum crystals associated with the actinolite-thremolite grains that serve as sources of the calcium is observed (b). The BSE image and layered mapping of E stone in a mixed nitric and sulphuric acid solution. As the surface is eroded grains of quartz were exposed that leave small dents when they are lost (c).



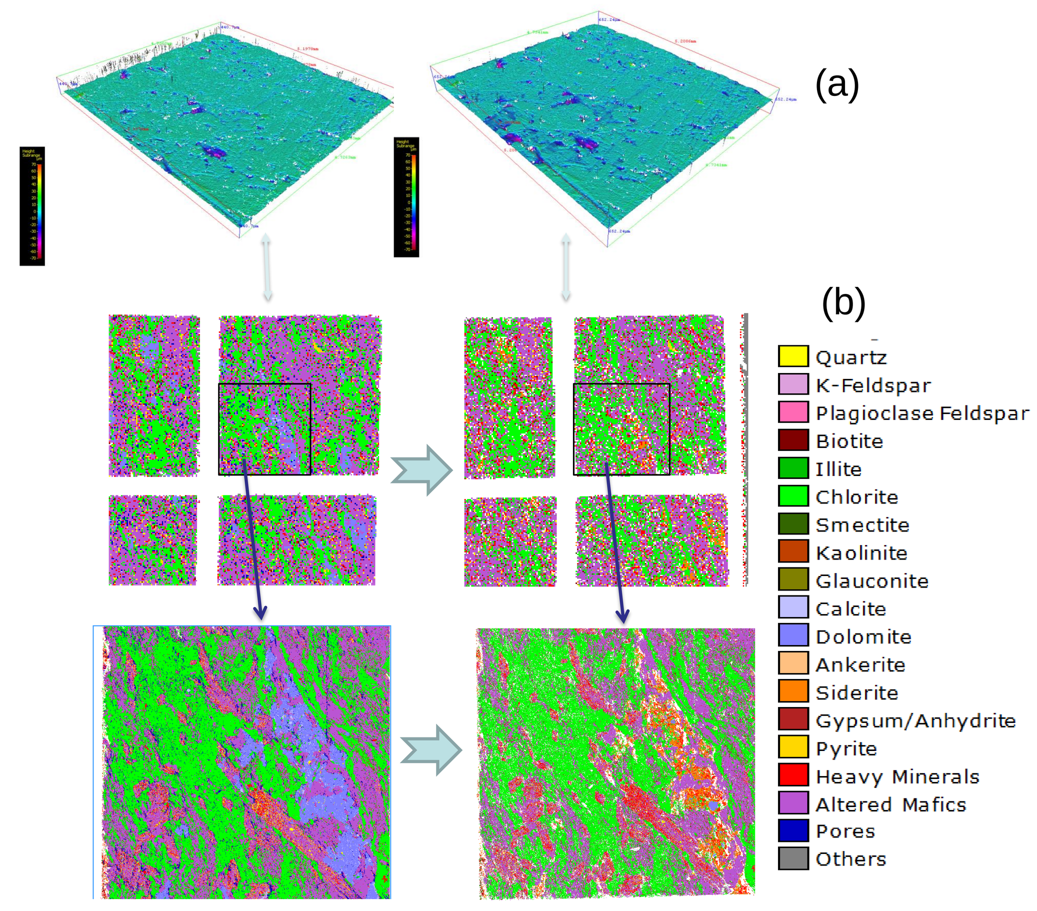
BSE image of yellowish spot in NG stone in nitric and sulphuric acid solution and the corressponding layered elemental mapping after the first round (a). The yellow colour is due to oxides of iron appearing as white in the elemental layered mapping. The chlorite appears greenish blue, the talc greenish, the dolomite as yellow and pyrite as red. (b) shows the layered mapping of a larger area than in (a) and the individual elemental mapping. The pyrite was not affected much by the acidic treatment except at the interface.



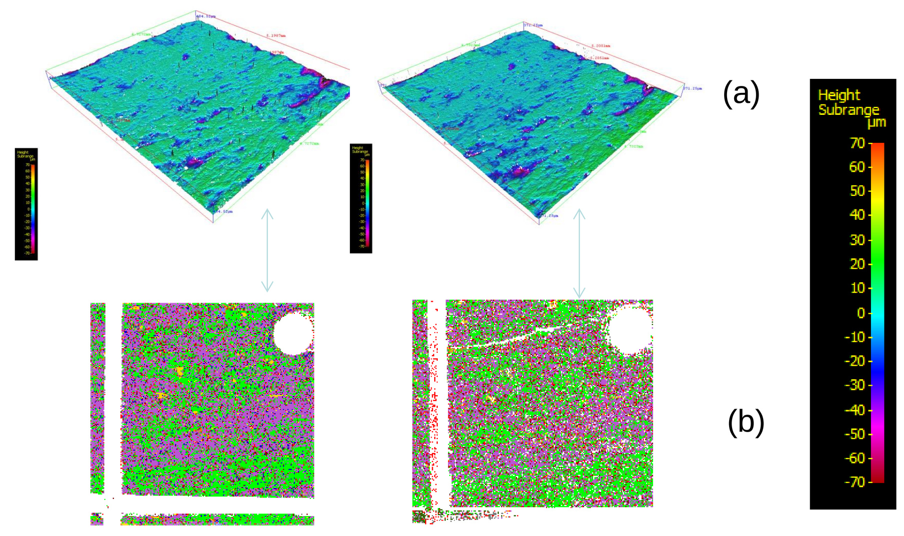
Fluorescence imaging of thin-section samples prepared by embedding in a resin containing fluorescent compound. The cracks and fissures are apparent much more enhanced in NB stone (a). Along with the relatively thinner fissures, the fluorescent components of NG (b) are also visible. The thin-section from E (c) shows the intergranular spaces. The microscopic image of E and the NB under crossed polars of PLM are shown in (d) and (e) respectively.



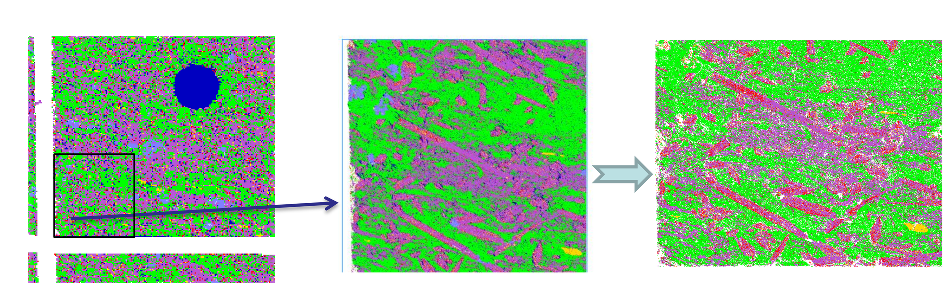
3D laser microscope images of the surfaces of E stone in sulphuric acid solution before weathering and after second round (from left to right) (a). The dolomite rich site appears more exposed as the calcite is eroded (a). The mineral map of the same stone above from QEMSCAN. The left most is at low magnification (resolution of 100x100 micron) where as the middle and the right images at high magnification (10x10 micron resolution) (b). Dolomite appears as darker blue while calcite as light blue. The mineral map of NB stone before and after weathering in sulphuric acid solution in the second round is shown in (c). The loss of dolomite, increased coverage of gypsum and appearance of large cracks are observed.



3D laser microscope images of the surfaces of NG stone in sulphuric acid solution before weathering and after second round (from left to right) (a). The dolomite is associated with eroded sites (a) The mineral map of the same stone above from QEMSCAN (b). The ones at the top are at a resolution of 100x100 micron where as the bottom images are at 10x10 micron.



3D laser microscope images of the surfaces of NB stone in nitric and sulphuric acid solution before weathering and after second round (from left to right) (a). The greater loss at the edges compared to the inner parts is observed. The mineral map of the same stone above from QEMSCAN at low magnification (100x100 micron resolution) .



The mineral map of NG stone in a mixture of nitric and sulphuric acid solutions at low magnification (100x100 micron resolution) left and high magnification (10x10 micron resolution) the middle and the right. The comparison is between the stone composition before the accelerated and after the second round. Loss of dolomite and conversion of actinolite – tremolite elongated grains due to gypsum formation are indicated. The chlorite appears less affected by the acid action.

Acknowledgement

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