

## Petro-chemical and physical investigations on the “Santa Pudia Calcarenite” (Andalusia, Spain): New hints for the prevention and conservation of calcarenitic building materials

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An experimental mineralogical, chemical and petro-physical study of the “Santa Pudia Calcarenite” (Andalusia, Spain) was carried out in order to get information on its physical properties and behaviour to weathering processes, useful for a full understanding of its degradation and decay mechanisms. This bioclastic calcarenite was used for the building of the Granada Cathedral (Spain), but issues of a much broader interest may rise by taking into account that it is widely employed in the Andalusian architectonic heritage.

Two cromatic varieties (white and yellow) from the Santa Pudia quarry and a black crust-bearing sample from the Cathedral were analysed by means of optical microscopy, XRD and SEM-EDS. Porosimetric analyses, hydric tests (water absorption and drying), ultrasonic pulse velocity measurements, accelerated ageing tests (including alternating cycles of freezing-thawing and humidity-drought, salt crystallization and efflorescence in the absence and in the presence of different crystallization inhibitors) were also performed. The salt crystallization process was real-time monitored by means of ESEM.

Results showed that the Santa Pudia calcarenite has a poor degree of pore connectivity probably due to an intra-particle microporosity, thus not allowing water to easily flow within the rock, although the open porosity ranges between 25% and 30%. Accelerated ageing tests highlighted a scarce resistance to alternating cycles of freezing-thawing and to salt crystallization. Efflorescence tests put into evidence that none of the tested additive is an efficient inhibitor for salts (NaNO<sub>3</sub>) nucleation and crystallization. However, citric acid is able to reduce the total amount of NaNO<sub>3</sub> efflorescence, enhancing the crystallization within the porous system, with a pressure exerted by salt crystals within pores lower than in the absence of additives.

The complete characterization of the Santa Pudia calcarenite presented here, with some possible implications also for other comparable calcarenites, puts forward new clues for preventing or, at least, slackening the trasformations induced by degradation mechanisms, salt weathering in particular, which would inevitably alter the aestheticism of the heritage.

## Mg-Fe<sup>2+</sup>-Fe<sup>3+</sup>-Al-Si-O phase relations at lower mantle conditions: Lack of evidence for Fe-disproportionation

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Experiment and theory show that the charge-coupled substitution  $\text{Fe}^{3+}\text{Al}^{3+} \leftrightarrow \text{Mg}^{2+}\text{Si}^{4+}$  is highly favored in Mg-perovskite, with Fe<sup>3+</sup> on the large Mg-site and Al<sup>3+</sup> on the smaller octahedral site [1-3]. This substitution is postulated to be so favourable that in the presence of (Mg,Al) perovskite, Fe<sup>3+</sup> will form by the disproportionation reaction  $3\text{FeO} \leftrightarrow \text{Fe}_2\text{O}_3 + \text{Fe}^0$  [1]. This reaction would produce coexisting (Fe<sup>3+</sup>, Al<sup>3+</sup>)-rich perovskite and iron metal in the lower mantle. If correct, FeO disproportionation provides a mechanism for the ‘self-oxidation’ of the mantle during core formation, and may help explain the siderophile element geochemistry of the mantle [1, 3]. Here, we investigate perovskite phase relations in the system Mg-Fe<sup>2+</sup>-Fe<sup>3+</sup>-Al<sup>3+</sup>-Si-O and report on laser-heated diamond anvil cell experiments at 30-100 GPa and 1500-2500 K. Run products were analyzed using synchrotron X-ray powder diffraction.

Experiments along the join MgSiO<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> up to ~70 GPa show a considerable solubility (>25 mol%) of Fe<sup>3+</sup> into perovskite via the substitution  $2\text{Fe}^{3+} \leftrightarrow \text{MgSi}$ , requiring that Fe<sup>3+</sup> occupies the octahedral site in Al-free systems. Unit cell volumes increase slightly with increasing Fe<sub>2</sub>O<sub>3</sub>, and the perovskite structure distorts mildly compared to distortion caused by Al<sup>3+</sup> or coupled Fe<sup>3+</sup>Al<sup>3+</sup> substitution. New experiments along the join MgSiO<sub>3</sub>-FeAlO<sub>3</sub> show a maximum FeAlO<sub>3</sub> solubility between 25 and 50 mol% at 70 GPa.

We made compositions in which enough FeO was added on a molar basis to MgSiO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> glasses for complete substitution via  $\text{Fe}^{3+}\text{Al}^{3+} \leftrightarrow \text{MgSi}$  should all the FeO disproportionate. Perovskite, ferropericlase and stishovite coexist in a composition with ~23 mol% Fe+Al at 35 – 60 GPa (~ 2000 K). In a composition with ~ 50 mol% Fe+Al, perovskite coexists with a ferrite-structured phase (± stish. or ferroper.) at similar P-T conditions. These results are explicable by quaternary phase relations in the reduced system MgO-FeO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. In contrast, if iron disproportionation were occurring then a Fe<sup>3+</sup>-Al<sup>3+</sup>-rich perovskite would coexist with pure iron. Calculations show that even 1 mol% iron metal should be detectable by diffraction, yet we see no clear evidence of metallic iron in any diffraction pattern. Our results indicate that above the maximum solubility of Fe<sup>2+</sup> in aluminous perovskite, stishovite + ferropericlase are stabilised and phase relations remain quaternary.

### References

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