

# Building stones explained 7

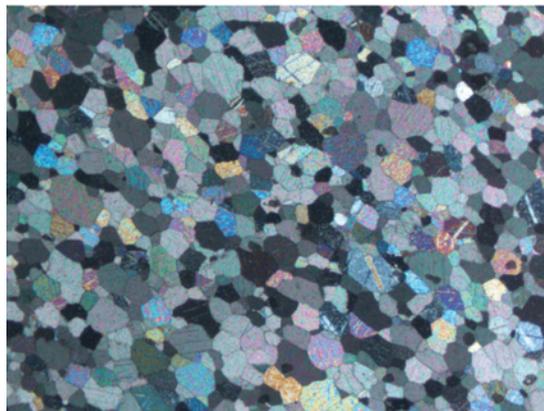
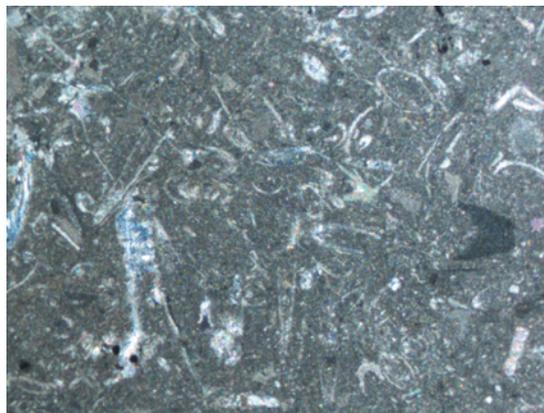


## Serpentinite

Serpentinites are metamorphic rocks formed from the alteration of ultramafic igneous rocks. Their precursors largely consist of clinopyroxene, orthopyroxene, olivine and a member of the spinel group, along with other accessory minerals. Serpentinization can be produced through the percolation of fluids of different origins. The transformation gives rise to other rocks, serpentinites, that are characterized by a high-water content mineralogy (serpentine) and, sometimes, remnants of the original phases. However, serpentinites may also undergo a subsequent carbonation process, transforming most of the mineral phases into carbonates. This is why confusion may arise when dealing with these rocks in the industrial sector, where geologists are not often involved. Serpentinites are often found in natural stone catalogues under the name of 'green marble' and this can be misinterpreted by builders and architects, causing misuse of this rock as an ornamental stone.

Geology is a multidisciplinary science and different scientific approaches are used in the characterization of rocks as dimension stone: mineralogical and geochemical aspects, together with the evaluation of deformation structures and physical-mechanical behaviour should be taken into account when assigning a specific use to a rock. In the case of serpentinites, all these scientific aspects have the common objective of a complete characterization aimed at finding the different uses they might be put to, ranging from construction to CO<sub>2</sub> storage, hence avoiding the conflict that could arise from their misuse. Unfortunately, expert advice is not always taken into account in exploring the possibilities of these natural resources.

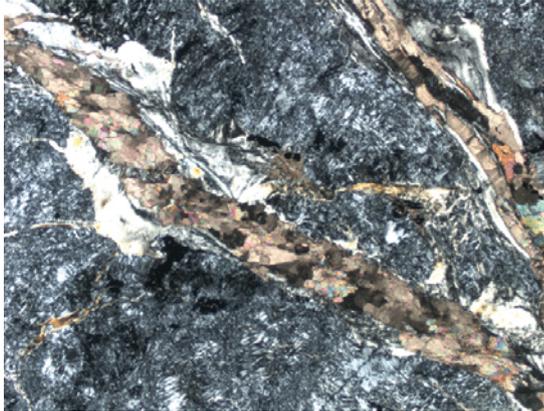
Our ancestors knew about the construction value of rocks merely by looking at them. Rocks were selected because of their quality and the uses they were to be put to. Transport logistics were very restricted (or nonexistent) and local stone was used both for civil architecture and historical buildings. However, when roads were built and transport by sea, train and motorways was developed and improved, rocks could be moved easily from one place to another; indeed, even from one part of the world to the other. The criteria for choosing a particular building material changed and quality was sometimes relegated to the trends of the times or the whim of architects. From



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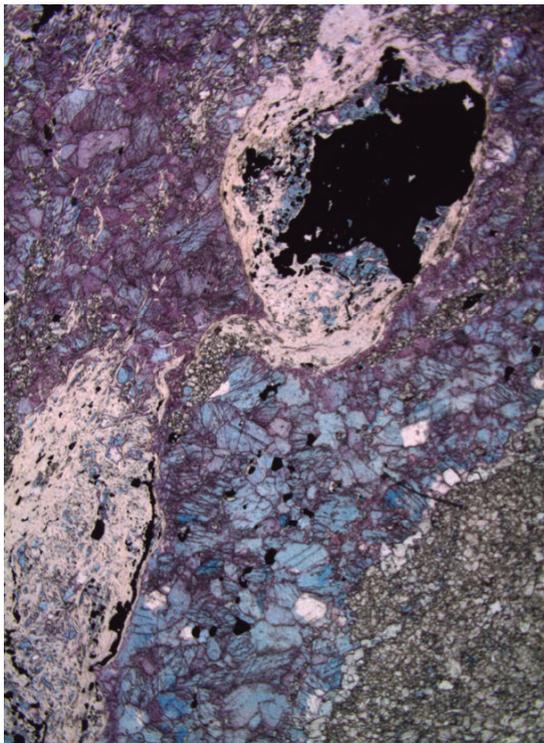
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**Fig. 1.** Thin sections under the microscope showing textures of two different carbonate rocks: the fossiliferous Leithakalk Limestone (Czech Republic) and a pure white marble from Carrara, Italy. Both are used as ornamental stones.



**Fig. 2.** Carbonates filling shear zones.

that moment, geology started to play an important role in the construction sector, but the application of expert knowledge has never been mandatory. Deciding on the kind of rock is a decision to prevent, first, an unpredicted deterioration of the built infrastructure, and second, legal problems associated with the misuse of the rock in building construction. It is common for architects to decide on which rock to use based only on the external features of the stone. However, in a natural stone catalogue two different rocks may be found under the same name, mainly because the definitions that engineers and architects have been giving to building materials do not follow any scientific criteria. For example, in the industrial sector marble is defined as ‘any rock that admits being polished’. Under this definition many different rocks could (inappropriately) be included. Limestones are



**Fig. 3.** Thin section showing magnetite formation due to an excess of iron in the rock. Carbonates are tinted and the blue colour indicates the existence of Fe-rich calcite.

sold as marble although they are sedimentary rocks, in contrast to the metamorphic origin of true marbles. Limestones and marbles are made up of calcite and other carbonates, but the latter exhibit a high degree of recrystallization of the carbonate phases, producing a special texture that lends greater strength to the rock, which can therefore be used in a broader scenario than limestones. These are sometimes very fragile, preserving even the most detailed biological content that gave rise to them.

The same explanation can be given to see the differences between serpentinites and marble (Fig. 1).

### Serpentinite is not marble

Serpentinites are metamorphic rocks formed by the alteration of magnesium-rich ultramafic igneous rocks due to the influence of fluids. In fact, serpentinites are characterized by a content of water higher than 13 per cent in their chemical analysis (for a comparison, fresh granite and pure marble have less than 2 per cent). The fluids producing the serpentinization may have different origins: from deep sites, rising up through shears (Fig. 2) and veins and producing a hydrothermal alteration of the previous ultramafic rocks, or shallow settings or even a meteoric origin, producing a different alteration process or weathering of the high-magnesium precursor. The result of the transformation will depend on the composition of the fluid but also on the composition of the previous ultramafic rock. Serpentine is a magnesium-rich phyllosilicate and hence only magnesian phases will be transformed into serpentine as the secondary phase: magnesium-olivine and pyroxene are the common phases susceptible to being converted. However, during the serpentinization of rocks, other phases are produced as secondary products of the transformation. When there is an excess of magnesium in the original mineral phases, magnesium-carbonate (magnesite and/or dolomite) will be produced as well as serpentine. Nevertheless, for this to happen, calcium and  $\text{CO}_2$  are needed in the reaction.

Only specific pyroxenes rich in calcium in their structure would be able to follow this transformation. If magnesium is in great enough excess, a magnesium oxide (magnetite) will be produced (Fig. 3) as well as magnesite (and dolomite). Thus, at this point we have a rock made up of serpentine plus carbonate (plus other minor phases). If the rock undergoes a long history of transformation, most mineral phases will be transformed into carbonates. We will then have a carbonated rock that is no more than a carbonated serpentinite. But it is still not a marble.

**Table 1.** Chemical composition of two serpentinites under different stages of the carbonation process

	Verde Macael	Verde Pirineo
SiO <sub>2</sub>	0.17	38.99
TiO <sub>2</sub>	0.01	0.00
Al <sub>2</sub> O <sub>3</sub>	0.00	1.06
FeO	0.28	8.06
MgO	0.07	38.09
MnO	0.15	0.05
CaO	49.64	0.11
Na <sub>2</sub> O	0.06	0.05

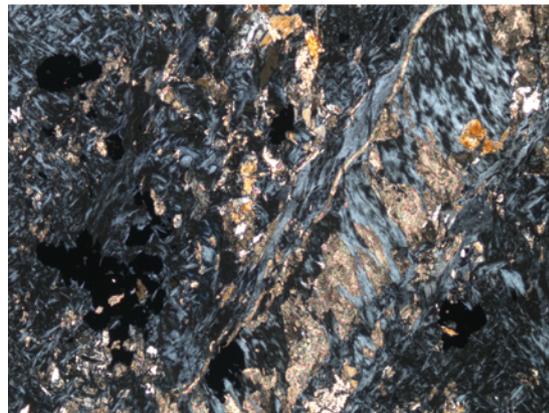
Verde Pirineo and Verde Macael are commercial names.

### Carbonation of serpentinites

The carbonation of serpentinites can occur through two different processes: (1) the precipitation of carbonates in the shears and fractures of the serpentinite; and, (2) transformation of serpentine into carbonate through specific reactions.

Serpentinite is a very fragile rock because it is produced from the pervasive alteration or weathering of a previous, dense rock. When hydration reactions occur and produce the mineral transformation, the volume of the rock expands, producing deformation and changes in the original textures and hence a weakness in its mechanical behaviour. The product is a highly porous rock with a tendency to shear and break. If ideal conditions are reached (e.g., high-CO<sub>2</sub> fluids with calcium have access to these fractures) carbonates precipitate, filling these structures. This is a clear indication of the significant volume gain in the process of serpentinization, when extensional fractures were produced.

Serpentine is present as three different polymorphs, depending on the temperature and pressure conditions of its formation. These polymorphs are lizardite, antigorite and chrysotile. There is no evidence of any of these phases being more able than the others to become transformed into carbonates. However, the amount of magnesium and calcium in the precursor rock will be decisive when the serpentine is trans-

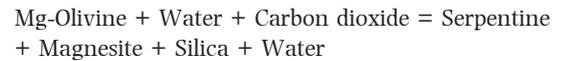
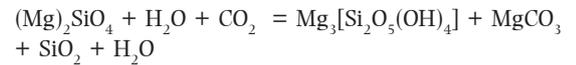


**Fig. 4.** Replacement of serpentine by carbonate.

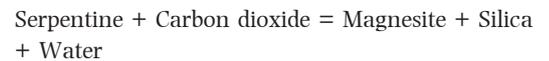
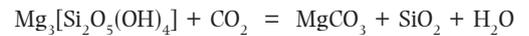
formed into carbonate (Fig. 4), first to magnesium carbonate (magnesite and/or dolomite) and then to calcium carbonate (calcite) if an excess of calcium is available. In this case no precipitation occurs but the replacement of the serpentine by the carbonated phases does take place.

This replacement can be explained if the main transformed original mineralogy is made up of Ca phases instead of Mg minerals. In this case, the carbonate minerals in these rocks were probably formed by the reaction between CO<sub>2</sub> in the circulating sea-water and Ca in the minerals.

Different reactions can take place in a carbonatization process. Some involve the breakdown of relict olivine, to give antigorite and magnesite.



or



In any case, a major percentage of the rock will be made up of carbonates. In this case, replacement is produced by the precipitation of carbonates within a volume formerly occupied by serpentinite minerals, no differences in volume during this transformation being involved. If later fluids enriched in calcium affect an already carbonated rock, magnesium carbonate can be transformed into calcium carbonate (calcite) or the remaining porosity can be filled out by this new carbonate phase, indicating different sequences in the carbonation process under different chemical conditions. In any case, the geochemical characterization of carbonated serpentinite is equivalent to any carbonated rock of any origin. Here is where the incorrect characterization can take place.

### Decaying of serpentinites

Natural stone changes when it is taken from the outcrop to the building under construction. This is a normal occurrence, since the rock may be taken from one environment and placed in a very different one. Sometimes it passes from dry conditions to wet, but the opposite may also occur. If a serpentinite is placed in a humid atmosphere, its behaviour will differ depending on whether it is carbonated or not. However, its behaviour will also differ depending on the type of carbonation of the serpentine. That is, if the rock has undergone a complete transformation to carbonates,

**Table 2.** Physical properties of the serpentinites from Table 1 as compared the properties demanded by the ASTM American directive

Physical properties	ASTM requirements	Verde Macael	Verde Pirineo
Absorption (%) Ext./Int.	0.20 max./0.60 max.	0.20	0.93
Density (kg/m <sup>3</sup> )	2.560 (min)	2.810	2.700
Compressive strength (MPa)	69 (min)	82.7	34.46
Flexural Strength (MPa)	6.9 (min)	13.5	5.92

**Fig. 5.** Renovation of store in Vienna, 2004; the same, renovated, store in Vienna, 2010. One tile has been replaced and, to homogenize the colour, the other tiles have been varnished (unsuccessfully).



**Fig. 6.** Genoa's Cathedral façade, made of white, red and green 'marble'.



these carbonates act as a cement for the serpentinite and the strength of the rock is increased. However, if the serpentinite is sheared and the shears are filled with carbonates, the response to weathering once it has been emplaced in a building will be far worse than in the first case, because the rock slab will behave as two lithologies with two different behaviours; the serpentinite will tend to deteriorate faster than the carbonated veins and the rock will break along those structural limits.

### Consequences for architecture

Serpentinites can be used for different purposes, but due to their physical-mechanical characteristics, with a very high absorption coefficient and high porosity, they should be avoided for uses where fluids will be involved: external paving and walling and the lower-most structures of buildings. However, these geotechnical characteristics may change if the serpentinite is transformed into carbonates by replacement. In this case, the carbonate acts as cement, affording the carbonated serpentine greater strength and reducing its absorption coefficient. Several industrial companies document these properties, but the rock is still misused because, since it is not a marble, remnants of other minerals can be found and the behaviour of the rock will not be homogeneous either for structural use or, when polished, for ornamental purposes (Fig. 5). Additionally, since carbonates replace serpentine, although there is no recrystallization involved, depending on its use the rock may undergo a dramatic deterioration.

If these events occur in civil architecture or when serpentinites are only used for ornamental purposes—although problematic from an aesthetic point of view—solutions can be found through a reasonable (or unreasonable) reconstruction.

However, if the rock fails to be properly characterized when used in the restoration of historical buildings, there would be a major impact because the serpentinite will follow its own evolution, and weathering will leave a footprint in the restored part, which may contrast strongly with the original material. Let us take, for example, the polychrome façade of the Italian cathedrals (e.g. Florence, Genoa; Fig. 6). In their construction, the builders of Italian façades used white, red and green marble; only the white marble from Carrara being pure. The red type is a limestone and the green one is serpentinite, originally from Prato. Florence underwent a disastrous flood in 1966 and a complete restoration was made. However, the quarry in Prato had closed down and no mining was taking place at the time of the restoration, and another 'green marble' was used: the Verde Alpi. Verde Alpi is also a serpentinite, but now we know that serpentinites can be very different in

mineralogy, texture and structures, including the diagenetic changes that may have taken place during their evolution in the outcrop. Several changes may occur during their evolution as an ornamental stone on Florence's cathedral façade and in this case misuse of the wrong materials in the restoration could give rise to problems.

### Suggestions for further reading

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