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Variations on the silica theme: Classification and provenance from Pliny to current supplies

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Over recent decades, numerous studies have highlighted the importance of opal, chalcedony and quartz varieties, chiefly in volcanic, but also in metamorphic and sedimentary environments. The focus is to define accurately their structures, composition and properties, as well as to identify the factors controlling the formation and the ageing of different forms of silica. In the field of archaeological sciences efficient discriminants are the bases from which the origin and provenance of materials may be traced. Substantial efforts were made in the attempt to combine geochemical, mineralogical, petrographic and geological features with archaeological and archaeometric information. However the results show that data integration is complicated, and several unanswered questions remain. On the one hand, archaeological research has focused on technological and ethnographic aspects, mainly concerning use-wear and heat-treatment studies. Mineralogical characterization has often been limited to the identification of the material, frequently by Raman microspectroscopy alone. On the other hand, the Earth sciences have provided basic mineralogical, crystal-chemical and geological knowledge, but failed to provide a systematic data collection of sources and their geochemistry. As a consequence, large gaps persist in the identification of archaeological opals, chalcedonies and quartz varieties, and in the geographic mapping of possible sources.

In this context, the present review aims to summarize the current academic debate on such issues, possibly to encourage further work in the field. After a brief introduction to terminology, the structure of opals, their colours and properties are discussed, followed by an introduction to silica dissolution/precipitation and opal-formation processes.

The next section reviews the information available on use of opals and provenance from historical sources, mainly Pliny the Elder, followed by a short list of ancient and modern opal supply areas, together with a (necessarily incomplete) summary of the geological and geochemical information.

The discussion then encompasses chalcedony, agate and chalcedony varieties (carnelian, sard, onyx, sardonyx, chrysoprase, Cr-chalcedony, 'gem silica' or 'chrysocolla chalcedony' and heliotrope), following the same scheme as was adopted for opals. Terminology, distinguishing features, formation conditions, information derived from Pliny's books, past and current supply areas and, finally, archaeometric provenance issues are addressed for each type of material. As for chalcedony, a comprehensive note on moganite has been included.

The next section focuses on chert, flint and jasper. Given the large amount of materials available on this topic, the present review must necessarily be considered introductory and partial. The discussion aims to provide useful indications on how to distinguish chert from flint and chert from jasper; secondly, the information provided by Pliny and the archaeometric state of the art on these materials is reviewed.

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The last section examines quartz varieties: hyaline quartz (rock crystal), milky quartz, smoky quartz, rose and pink quartz, amethyst, citrine, prasiolite and blue quartz. An exhaustive mineralogical discussion on quartz is beyond the scope of this review; conversely a review of the historical information is provided, together with a brief list of major supply areas, a summary of the archaeometric studies performed on these materials, as well as an indication of the geological literature which can be used proficiently for provenance studies.

1. Classifying opal, chalcedony and quartz varieties

"*Nec est aliud difficilius quam discernere haec genera*" *(Pliny N.H. 37, 98)*
(Nothing is harder than the attempt to distinguish the varieties of this stone)

The terminology usually adopted for the characterization of natural silica-based materials may be a potential source of confusion, as it combines well established but somewhat vague terms (*e.g.* carnelian, sard), technical terms (*e.g.* chalcedony and quartzine) and commercial terms (*e.g.* fire opal).

A wider knowledge of these materials (*e.g.* of factors controlling the formation of different forms of silica) would be needed in order to provide a systematic review of their nomenclature. Table 1 illustrates schematically how to distinguish opal from chalcedony and quartz varieties, using broad distinctions and without taking into account the possible variations due to secondary processes, such as recrystallization.

Among others, the terms "silica sinter" and "jasperoid" were not included in the table as their use is confined generally to geological studies on hydrothermal alteration. Silica sinter indicates those deposits which formed by precipitation from aqueous solutions and where silica prevails over all other possible components (travertine represents its carbonate equivalent). Conversely, the name jasperoid has been applied to "epigenetic siliceous bodies formed largely by replacement, thus excluding cherts that may have formed in lime muds either syngenetically and diagenetically" (Lovering, 1962, on the characteristics and distribution of jasperoids in American carbonates). A different case is presented by aventurine which is not a mineral in the strict sense. This is generally described as a quartzitic rock, coloured green by fuchsite.

2. Opal-A_N, Opal-A_G, Opal-CT, Opal-C

2.1. An introduction to their structures, colours and properties

The distinction between opal-A_N and opal-A_G was introduced by Langer and Flörke (1974), based on small-angle X-ray and neutron scattering experiments.

The network-like opal-A_N (rarely used as a gem) is characterized by a water-containing glass-like structure (Flörke *et al.*, 1973), indicated by diffuse scattering of X-rays and neutrons at small angles. Previously called hyalite, opal-A_N is far less widespread than the opal-A_G variety and is typically botryoidal (generally forming a millimetric crust on volcanic rocks), colourless and shows strain-induced birefringence under the polarizing microscope (Flörke *et al.*, 1985; Graetsch, 1994; Gaillou *et al.*, 2008a).

Table 1. Basic criteria for the distinction between opal, chalcedony and quartz varieties. Grain size can be fixed arbitrarily as follows: macro- (crystals visible to the naked eye, >30 μm), micro-crystalline (<30 μm) and cryptocrystalline (<1 μm). Prev. = prevalent; min.= minor contents; ev. = eventual.

	Macrogroup	Growth form	Phases	Varieties	Main features
High solubility Low structural order	OPAL	Amorphous	–	Opal-A$_N$	Prev. hyalite. glass-like structure.
			–	Opal-A$_G$	Close-packed arrangement of homometric spherical particles of amorphous silica (150−350 nm), with a long-range order not exceeding ~9 Å
		Amorphous and microcrystalline	Cristobalite and tridymite	Opal-CT	Prev. lussatite. Crystalline or rather "para-crystalline". Ordered and disordered inter-stratifications of cristobalite and tridymite layers. Silica nanograins with different degrees of organization. Includes "fire opal".
			Mostly cristobalitic. Presence/absence of tridymite controversial	Opal-C	Prev. lussatine. Higher degree of crystallinity and lower disorder in the crystal structure with respect to opal-CT.
	Chalcedony (prev.), opal (ev.), quartz macrocrystalline (last filling)	Amorphous to macrocrystalline	Chalcedony + moganite/quartzine (+ opal) (+quartz)	Agate	Colours: red, orange, brown, yellowish, purple, white, grey, green and, more rarely, blue. Must be banded. Possible causes of banding: (a) alternating phases of activity and rest in the crystallization process, (b) Fe oxide 'self-purification' process during crystallization, (c) Al^{3+} and Fe^{3+} substitutions for smaller Si^{4+} and (d) textural and structural changes.
	CHALCEDONY	Fibrous microcrystalline and nanocrystalline (prev.), amorphous (ev.)	Chalcedony + moganite/quartzine	Carnelian	Orange variety
				Sard	Dark orange variety
				Onyx	Black and white variety
				Sardonyx	Brown and white variety
				Chrysoprase	Apple green variety (Ni-based chromophore)
				Cr-chalcedony	Emerald green variety (Cr-based chromophore)
				Heliotrope	Green variety dotted with small, hematite red, blood-like spots
	Quartz (prev.), chalcedony (min.)	Granular microcrystalline (prev.), fibrous microcrystalline (min.)	Chalcedony + moganite/quartzine + quartz	Chert	Used in geological papers. Broad term indicating large bodies of white or lightly coloured rocks. Mainly in "soft" carbonates.
				Flint	Mainly used in archaeological papers. Darker variety of chert. Nodules in chalk and marl.
Low solubility High structural order	QUARTZ	Macrocrystalline granular	Quartz	Rock crystal	Transparent variety
				Milky quartz	Milky appearance due to fluid inclusions.
				Smoky quartz	Smoky appearance due to aluminium (Al^{3+}) impurities substituting silicon (Si^{4+})
				Rose quartz	Rose variety. Colour due to Fe^{2+}–Ti^{4+} intervalence change transfer in dumortierite
				Pink quartz	Pink variety. Colour due to Al-O^{-}-P hole centres induced by ionizing radiation.
				Amethyst	Purple variety. Colour due to (mainly) trivalent Fe replacing Si in its tetrahedral sites
				Citrine	Rare yellow variety. Colour due to trivalent iron (Fe^{3+}) and colour centres often associated with Al impurities
				Prasiolite	Green variety (≠ from prase). Radiation-induced colour variant of quartz (iron chromophore).
				Blue quartz	Rare blue variety. Colour due to Rayleigh scattering by submicron-sized inclusions.

In the gel-like opal-A_G variety (generally synonymous with opal-A), the basic structure comprises a close-packed arrangement of homometric spherical particles of amorphous silica (150–350 nm), with long-range order not exceeding ~9 Å (Graetsch, 1994; Rossmann, 1994).

The presence of variable water contents (1–8 wt.%) characterizes both species (further details in Langer and Flörke, 1974), reducing their refractive index and density. Mostly molecular, water is lost largely at 200ºC and is almost absent at 400ºC (Jones and Segnit, 1971; Langer and Flörke, 1974). In opal-A_G water fills the interstices between the spherical silica particles and the scattering intensities imply interparticle interferences superimposed on diffuse scattering (Langer and Flörke, 1974; Graetsch and Ibel, 1997). Both the common ("potch") and the precious opal are mainly included in this variety, the distinction being in the absence or presence of the play-of-colour.

In precious opals, the play-of-colour is caused by diffraction of light by the randomly faulted, cubic- or hexagonally-packed spheres of amorphous silica (150–350 nm); schematically, the greater the diameter of the particles, the greater the lattice parameter and the grating which establish the range of colours diffracted by the opal (Sanders, 1964, 1968; Sanders and Darragh, 1971; Rossman, 1994 with references therein). Small spheres will give rise to blue and violet colours, while large spheres will be responsible for red and orange colours. In sedimentary environments, gravitational settling has generally been considered as the main factor controlling the formation of ordered lattices of spheres in the fractures and pores of the host rocks (Darragh *et al.*, 1966; Rey, 2003; Pecover, 2007; Gaillou *et al.*, 2008a, Pewkliang *et al.*, 2008), however, Liesegang and Milke (2018) oppose this reconstruction claiming that "gravitational settling/ordering is the exception rather than the rule".

In common opals, the lack of play-of-colour is caused mostly by the non-uniformity, inappropriate packing and dimensions of silica sphere (Sanders and Darragh, 1971) but also by the complete filling of the interstices by silica cement (Graetsch, 1994). Gaillou *et al.* (2008a) noted that: (1) diffraction was inhibited by a variation of only 5% in sphere diameters; (2) imperfectly shaped spheres occurred relatively commonly; (3) the minimum (~140 nm) dimensions range of the sphere in order to diffract light was still applicable, while doubts remained about the maximum value of ~650 nm; and (4) the effect of several compaction features was significant.

Within the aforementioned dimensional range of the spheres, the development of a non-uniform array seems to be controlled mainly by the deposition temperature (see Section 2.3.) and the silica concentration; in fact, a high concentration of spheres has limited freedom of movement and makes regular stacking nearly impossible (Filin *et al.*, 2003). In this regard, it is worth noting that the absence of voids seems to represent a characteristic feature of Australian opals, in contrast to the Californian ones from the Lead Pipe Springs and Last Chance Canyon deposits (Sanders and Dietz, 1967).

Unlike opal-A_G and opal-A_N, opal-CT is crystalline or rather "paracrystalline" (Smith, 1998). Previously known as lussatite (*i.e.* a variety of fibrous cristobalite defined in Mallard, 1890), opal-CT consists of silica nanograins (12–32 nm in size in Rice and Elzea, 1993, average of ~25 nm in Gaillou *et al.*, 2008a) with four different degrees of organization: (1) random; (2) arranged in fibres; (3) arranged in platelets; or (4) arranged in lepispheres (Gaillou *et al.*, 2008a). The random arrangement (type 1) characterizes most "fire" opals (*i.e.* transparent and bright orange) which, characteristically, have nanograin diameters ranging ~10–~50 nm. The fibrous arrangement (type 2) is present in opaque pink opals, which possess fibres with diameters of ~20–25 nm and lengths of ~4 μm (see also the Mexican pink opal-CT associated with palygorskite in Fritsch *et al.*, 2004). Type 3 has nanograins arranged as platelets (with blades corresponding to the {111} or {001} forms of cristobalite and tridymite, respectively). They are typically ~25 nm thick and ~300 nm wide but their thickness seems to vary depending on their provenance (Graetsch, 1994; Gaillou *et al.*, 2008a). The lepispheres which characterize type 4 are almost equidimensional platelets intersecting at a nearly common centre, thus assuming a sphere-like shape. The lepispheres vary in diameter from ~250 to ~1000 nm and are generally embedded in a silica nanograin matrix. Gaillou *et al.* (2008a) found all the four types in Mexican opals, but only types 1 and 3 were present in opals from Australia, Ethiopia and Turkey; type 1 CT opals were reported from Brazil, Kazakhstan (an interesting review on precious and decorative non-metallic minerals from east Kazakhstan is in Chernenko and Chlachula, 2017) and Tanzania; type 2 opals from Peru; and type 3 from France, Madagascar and Venezuela.

As demonstrated by numerous authors (*e.g.* Mizutani, 1970, 1977; Jones and Segnit, 1971; Flörke *et al.*, 1975; Williams and Crerar, 1985; Elzea *et al.*, 1994; Graetsch, 1994; Guthrie *et al.*, 1995; Cady *et al.*, 1996; Nagase and Akizuki, 1997), opal-CT is characterized structurally by both ordered and disordered interstratifications of cristobalite and tridymite layers; the proportion of the two phases being largely cristobalitic (Jones and Segnit, 1971; Rice *et al.*, 1995) or largely tridymitic (Mitchell, 1967; Mitchell and Tufts, 1973; Wilson *et al.*, 1974; Elzea and Rice, 1996) or nearly equal (Flörke *et al.*, 1991; Graetsch, 1994; Guthrie *et al.*, 1995). Continuous attempts to model the structure of opal-CT have resulted in several authors proposing to distinguish a new tridymitic end-member – "opal-T" – from opal-CT, alongside the better-known opal-C (Eversull and Ferrell, 2008). Wilson (2014) proposed defining opal-CT as a "paracrystalline substance in which a disordered matrix predominates over the crystalline domains, as well as the proposition that these crystalline domains are largely tridymitic where opal-CT yields an X-ray diffraction (XRD) maximum near 4.10 Å".

With respect to opal-CT, opal-C (previously known as lussatine) is characterized by a higher degree of crystallinity and a lower disorder in the crystal structure (Elzea *et al.*, 1994). As is the case for opal-CT, the presence/absence of tridymite is still so controversial that some authors did not find it (Rice *et al.*, 1995), others indicated a very limited incidence of tridymite stackings (Jones and Segnit, 1971), yet others constrained the tridymite percentage to 20–30% with respect to cristobalite (Graetsch, 1994).

The content of molecular water present in the pores may be a discriminating characteristic, being ~1–3 wt.% in opal-C while ranging between 3 and 10 wt.% in opal-CT (Graetsch *et al.*, 1985, 1987; Flörke *et al.*, 1991; Cady *et al.*, 1996).

Using XRD, opal-CT and opal-C can be referred to mistakenly as α-cristobalite (Elzea *et al.*, 1994, Önal *et al.*, 2007) and, for this reason, Elzea *et al.* (1994) proposed observation of the (101) reflection. In opal-C, this appears intense, centred at near 4.0 Å and with a peak-width ranging from 0.222 to 0.453 Å. Conversely, in opal-CT, the same reflection would appear less intense, centred at near 4.07–4.10 Å, and with a peak-width ranging from 0.506 to 0.883 Å. The efficacy of heat treatments has been tested further by numerous authors, based on the simple concept that the (101) peak will shift for hydrated phases such as opals while it will not change position for α-cristobalite (Elzea *et al.*, 1994; Elzea and Rice, 1996; Hand *et al.*, 1998; Kahraman *et al.*, 2005; Önal *et al.*, 2007). Phosphoric acid (H_3PO_4) digestion was applied by Miles (1994), Kahraman *et al.* (2005) and Önal *et al.* (2007) in order to sharpen the (101) peak and to dissolve non-silica phases in bentonites and kaolins.

Lastly, as for colours, it is well established that impurities or mineral inclusions are responsible for the various hues such as the blue colour of Peruvian blue opals (Cu silicate; Rossmann, 1994; Gaillou *et al.*, 2008b), the yellow to orange, red or brown colour of many opals such as the "fire opals" (nanoscale inclusions of Fe-oxyhydroxides in Gaillou *et al.*, 2008b; Fe^{3+} in Rossmann, 1994) or a few Ethiopian opals (see *e.g.* Johnson *et al.*, 1996; Muyal, 2017; the latter-named for dyed specimens), and the opaque orange colour of Austrian "forcherite" opals (realgar; see Gaillou *et al.*, 2008b with references therein). The wide range of opal colours has led to the creation of a plethora of colloquial and trade names such as the aforementioned fire opals and forcherite (yellow, with realgar and orpiment), as well as the hydrophane (translucent in water), the milk opal and the honey opal (Duffin, 2006).

2.2. Silica dissolution and precipitation

Silica dissolution and precipitation control the formation of opal and of all silica varieties; therefore, this topic is referred to here but concerns quartz and chalcedony varieties too.

The main processes which can lead to large concentrations of dissolved silica are: (1) weathering of silicate minerals, which is generally considered to be the most effective process in terms of quantity levels; (2) dissolution of amorphous silica, which can be observed in certain sedimentary environments; (3) dissolution of quartz, which is less effective than the other processes, given the low solubility of quartz; and (4) hydrothermal alteration of Si-rich rocks, which produces large concentrations of silica but is confined within retricted geographical limits. Therefore, the most likely places where dissolved silica can concentrate are thermal springs and all those geological formations where silicate minerals are present and, as a consequence, weatherable.

As for hydrothermal fluids, there are many factors that can enhance, reduce or inhibit the deposition of amorphous silica from silica supersaturated solutions: (1) rapid cooling, generally associated with decompressional boiling; (2) pH changes, *e.g.* due to the mixing of different waters; (3) presence of dissolved salts; and (4) interaction between fluids and volcanic glass (Fournier, 1985). The deposition of amorphous silica is favoured by near-neutral pH and high salinity (Morey *et al.*, 1961; Makrides *et al.*, 1980; Crerar *et al.*, 1981; Weres *et al.*, 1982). In weathering environments, the rates of dissolution and precipitation of silica are slow and the system implicates "a complex of spatial and temporal conditions" (Thiry *et al.*, 2014).

Dissolution and leaching, followed by evaporation and concentration, are the basic processes but they can, however, be affected by multiple concomitant events. In this regard, the activity of microbes have been considered further, given their capacity to weather clay minerals and feldspars through the excretion of acids and enzymes (see *e.g.* Banfield *et al.*, 1999; Chen *et al.*, 2000).

In the oceans, the amounts of dissolved silica are extremely small (of the order of a few tenths of a ppm); in fact, silica is extracted and fixed by diatoms, radiolarians and sponges to form part or all of their skeletons but it cannot be precipitated inorganically. Similar amounts are present in rivers and groundwaters (12/18 ppm SiO_2; see White *et al.*, 1963; Garrels and Christ, 1965).

Neutral to slightly alkaline (*i.e.* basic) waters produce thick silica sinters while highly acidic waters (pH <3) form silica deposits; in the latter case, the presence of H^+ ions inhibits silica polymerization (Rothbaum *et al.*, 1979; Weres *et al.*, 1982). Acidic waters, from outer rocks or internal oxidation, may attack silicate minerals (*e.g.* feldspars) and cause the release of silica into the solution and the consequent supersaturation of the solution itself. The latter case may be neutralized and precipitate amorphous silica. It is possible, although infrequent, that highly alkaline waters may also cause high rates of dissolved silica in hydrothermal waters, due to their ability to favour the dissociation of silicic acid (Fournier, 1985).

As for the solubility of silica phases, it has been established that amorphous silica is more soluble than all other silica varieties and, similarly to all the other silica phases, its solubility is influenced by temperature, pressure, pH, type of dissolved constituents in the solution (*e.g.* salts, organic compounds, *etc.*), particle size, structure and properties of the silica–water interface (see Dove and Rimstidt, 1994 for a comprehensive review of this topic).

To give a few examples relating to this topic, the solubility of amorphous silica in pure water at 100ºC is equal to that of quartz at ~225ºC (Fournier, 1985). With pH <9, the solubility is invariably ~120 mg/L SiO_2, while it increases strongly at pH >9 (Krauskopf, 1956). In the presence of most dissolved salts, below ~300ºC, the solubility decreases slightly, while it increases significantly in the presence of Na_2SO_4 at all measured temperatures (Marshall, 1980; Marshall and Warakomski, 1980; Chen and Marshall, 1982; Marshall and Chen, 1982a,b; Fournier and Marshall, 1983). This latter phenomenon has been correlated with the formation of silica-sulfate complexes (Marshall and Chen, 1982b; Fournier and Marshall, 1983).

Finally, the presence of organic compounds (Bennet, 1991) may further increase the solubility. Thiry *et al.* (2014), for instance, demonstrated that, in weathering environments, the dissolution of silica occurs mainly at the contact between organic compounds and organic-rich soils, while the precipitation of silica originates from pore waters.

2.3. Formation sequence

The debate on opal formation is part of a wider-ranging research topic regarding the diagenetic sequence which may develop from the highly soluble, non-crystalline opal-A to the crystallization of less soluble, highly structurally ordered quartz:

opal-A → opal-CT → opal-C → chalcedony → quartz

The procedures, constraints and timeframes in which this sequence proceeds have been the subject of numerous studies (*e.g.* Carr and Fyfe, 1958; Fyfe and McKay, 1962; Ernst and Calvert, 1969; Mizutani, 1970; Mukhopahyay and Chanda 1972; Murata and Nakata, 1974; Bettermann and Liebau, 1975; Flörke *et al.*, 1975, 1991; Murata and Larson, 1975; Murata and Randall, 1975; Kastner *et al.*, 1977; Murata *et al.*, 1977; Kano and Taguchi, 1982; Williams *et al.*, 1985; Jansen and Van der Gaast, 1988; Graetsch, 1994; Cady *et al.*, 1996; Lynne and Campbell, 2004). It is currently accepted that both the complete sequence (mostly in deep-sea deposits) and the direct formation of late phases (*i.e.* all except for opal-A_G) may happen, depending on formation environment (*i.e.* time, pH, salinity, solubility, saturation, temperature, presence of dissolved Mg, *etc*.). Authors do not agree about which factor should be the most determinant over all the others but it seems unlikely that a single factor may drive the entire sequence from the beginning to its end.

The degree of silica saturation in the solution is of fundamental importance in order to determine which type of silica polymorph will precipitate (Flörke *et al.*, 1982; Heaney and Davis, 1995). In fact, the greater the number of nuclei and crystal defects, the smaller the dimensions and degree of crystallinity of the silica variety that forms; on the other hand, the smaller the amount of silica in the solution, and the smaller the number of nuclei and crystal defects, the greater the dimensions and degree of crystallinity of the silica variety formed (Lee, 2007 with references therein). In this respect, the influence of temperature must not be underestimated. Low temperatures (~45ºC) – common in sedimentary environments – favour opal-A_G formation (see *e.g.* Rondeau *et al.*, 2004), while higher temperatures (around 170ºC) are necessary for opal-CT to deposit (*e.g.* Spencer *et al.*, 1992). Muldarisnur and Marlow (2017) have investigated opal formation from suspensions, while others (*e.g.* Carr and Fyfe, 1958; Rice *et al.*, 1995) have demonstrated experimentally that opal-A transforms to opal-CT/C during heating to temperatures of >1000ºC. Moreover, these data may further explain why opal-CT/C does not seem to have an opal-Ag precursor in numerous silica deposits of volcanic origin (see *e.g.* Graetsch *et al.*, 1994).

Lastly, Gaillou *et al.*, (2008b) observed that gem opal-CT was always found in volcanic environments while opal-A could have been found in both sedimentary (the most widespread) and volcanic environments. The study conducted by Gaillou *et al.* (2008b) showed how further geochemical investigations may distinguish between sedimentary (Ba >110 ppm, Eu and Ce anomalies) and volcanic opals (Ba <110 ppm, no Eu or Ce anomaly) and hence reconstruct the conditions of formation. In this regard, Chauviré *et al.* (2017a) have recently proposed a new method (near infrared signature) for the assessment of the geological conditions of opal formation.

2.4. Pliny on opals: description and provenance

Pliny's *Naturalis Historia* (1st century AD) reported on the then current state of mineralogy, petrography, geology and numerous branches of Natural Sciences. Due to its encyclopaedic nature, *Naturalis Historia* represents an ideal and indispensable starting point for Mediterranean Archaeometry.

Based on Pliny (*N.H.* 37, 80-84), only emeralds precede opals (*opalus*). Pliny (*N.H.* 37, 80) specifies that they display the "fires of the *carbunculus*" (*i.e.* carnelian or garnet), "the bright purple of the amethyst" and "the sea-green tint of the emerald", all combined together. However, still according to Pliny (*N.H.* 37, 83), the gemstone may also have shortcomings such as (1) a colour similar to that of the plant called *heliotropium* (*i.e.* intense purple if corresponding to the actual turnsole in the borage family, *Boraginaceae*; or green and red by analogy with the heliotope gemstone), or (2) a colour similar to that of rock crystal or even to that of ice, or (3) the presence of salt-like specks (or of salt efflorescence) and stains.

Pliny (*N.H.* 37, 81-82) further tells the story of the senator *Nonius* who was outlawed by Mark Antony for the sake of a precious opal, valued at 2,000,000 *sestertii*. It is possible to contextualize this information considering that, during the period of Caesar and Augustus, a senator had to have at least one million sesterces of annual income (Eck, 2000).

Pliny teaches us a method to recognise fakes and adds that opal was easily counterfeited in glass (*N.H.* 37, 83). The method would have consisted of observing the reflection of light through the stone orientated towards the sun. If the stone was fake, it would have shown a single colour; in contrast, the light would have passed through the real stone, shedding a bright light on fingers and showing different colours changing in the different parts of the stone.

The adoption of this method, along with the list of the defects that Pliny assigns to opal, seems to indicate that the name *opalus* corresponded to different types of stones. This is not surprising and may be confirmed by the mention of the "*paederos*" gemstone which, in Pliny's opinion, was the Greek term for opal while, according to others, it was a separate variety, corresponding to the Indian "*sangenon*" (*N.H.* 37, 84).

Pliny himself provides a controversial description of the "*paederos*" gemstone: initially as a sky-blue and purple opal, never showing the green tints of emerald (*N.H.* 37, 84), but some chapters later as a precious gem, characterized by a rock-crystal-like transparency, a sky-green tint, a glint of purple and the shining of golden wine (*N.H.* 37, 129-130). In this respect, it is interesting to note that today the "*Paederota Bonarota*" is a perennial herb characterized by blue-lilac blooms, which was named after the Plinian opals, forgetting perhaps that Dioscorides (40-90 AD) used this term for a type of *achantus* (*De materia medica* 4-74).

Greek mythology and Roman and Medieval superstition testify further to the worldwide popularity of opals. In Greek mythology, Zeus wept tears of joy which turned into opals when he won against the Titans. Centuries later, the Romans considered the opal capable of attracting large fortunes (similarly to the rainbow). The connection between opal and eyes (*ophtalmis lapis or Lapis optallion; LAPID.24*) was a Late Antique and medieval must (*ORPH.L.* 282-284; Kostov, 2008) and a commonplace of modern crystal therapy. No wonder then that opal was considered a “miracle” and the “Queen of gems” (Shakespeare, The Twelfth Night).

As for *opalus* provenance, Pliny indicates India as the sole producer (*N.H.* 37, 80) and, centuries later, Isidore of Seville (*Etimologiae*, 16) reports the same information (“*Nomen habet ex patria; sola enim eum parturit India*”) . Conversely, the supply areas listed for the *paederos* gemstone are more numerous (*N.H.* 37, 84, 130): Egypt (for a type of *paederos* called “*syenites*” or “*tenites*”), Arabia, *Pontus* (gems of lower quality; southern coast of the Black Sea, in Turkey), *Galatia* (*i.e.* central Turkey), Thasos (Greece), Cyprus and Thrace. In this instance, it is worth noting that these sites are more or less the same as those indicated for amethyst. The localization of the toponyms mentioned by Pliny is shown in Fig. 1.

2.5. Past and current supply areas

It is reasonable to suppose that the Carpathian (or “Hungarian”) opal sources were the main opal suppliers in Roman times (*e.g.* Frondel, 1962; Caucia *et al.*, 2013). The Slovakian mines were located between the districts of Prešov, Košicem, Červenica and Dubnik (Fig. 2). Considered the oldest mine in the world for opal mining, the site of Červenica (Slovakia) has been restored recently and operates in the field of Geotourism (Klamár *et al.*, 2017). Eckert (1997) also mentioned the town of Opalbanya, but he merely said that it must have been close to Dubnik.

Today, the major opal fields are located in Australia (Andamooka and Coober Pedy, New South Wales; Lambina and Mintabie, Queensland), Brazil, Canada (British Columbia), Ethiopia (Johnson *et al.*, 1996; Rondeau *et al.*, 2010, 2012; Chauviré *et al.*, 2017b; Muyal, 2017), Honduras, Mexico and the USA (Opal Butte in Oregon, Idaho, Nevada and Utah; for details of uraniferous opals from Spor Mountain and the Thomas

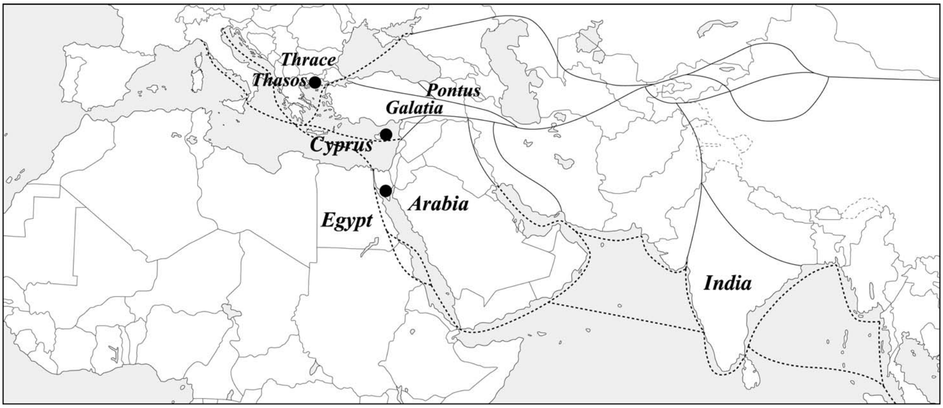

Figure 1. From the *Naturalis Historia* by Pliny the Elder: the distribution of *opalus* and *paederos*. The silk road and the principal maritime routes are shown.

Figure 2. Opal mines in Slovakia probably exploited during Roman times.

Range, Utah see Schindler *et al.*, 2017). Around the Mediterranean, sporadic occurrences have been registered in almost all countries but relevant deposits seem to be found in Bulgaria, Hungary, Czech Republic and Slovakia only (see also Sodo *et al.*, 2016). For a descriptive list of all modern mining sites and occurrences see Eckert (1997).

2.6. Opal provenance in archaeometry and information gained from the geological literature

In archaeometry, the provenance issue does not seem to concern opals, in fact specific publications are completely lacking. In this context, the Neutron Activation Analysis (NAA) investigations of 25 archaeological opals from Troy (Oregon, USA) represent an isolated case (Hess, 1996; Cummings *et al.*, 1989).

Papers available from the geological literature, by comparison, are slightly more numerous but still very few if compared to the worldwide occurrence of opals. Excluding materials from Japan as well as oceanic materials, geochemical analyses are available for at least 262 exemplars (see Appendix 1). Further spectroscopic investigations have been performed by Sodo *et al.* (2016). A further 50 samples of orange, yellow, honey, green, blue and pink opals and 18 samples of colourless opals from recognized fields in Australia, Peru, Mexico and USA must be added to the list (McOrist and Smallwood, 1995).

3. Chalcedony

3.1. Terminology and distinguishing features of chalcedony

For a long time the literature ignored the presence of moganite, or identified it with the different name of lutecite. This shortcoming meant omitting the effects of a determining variable, in relation to the physical and chemical properties of the material, as well as to its mode of formation and stability (*e.g.* solubility, geothermometers based on the concentration of dissolved silica, *etc.*).

Studying the evaporites of the Paris Basin, Michel-Levy and Munier-Chalmas (1892) introduced a ‘variety’ of length-slow chalcedony (*i.e.* with crystallites parallel to the *c* axis) in order to describe a silica phase intergrown with length-fast (*i.e.* crystallites stacked perpendicular to the *c* axis) chalcedony. This classification was further elaborated by Cady *et al.* (1998), who proposed to distinguish four microfibrous varieties: (1) chalcedony, with a parallel extinction and a length-fast elongation; (2) pseudochalcedony, with extinction subparallel to the *a* axis and a length-fast elongation; (3) quartzine, with a parallel extinction and a length-slow elongation; and (4) lutecite, with extinction subparallel to the *c* axis and a length-slow elongation. More precisely, the term lutecite was used when the *c* axis was at an angle of ~30′ with respect to the elongation direction of the fibres (Michel-Lery and Munier-Chalmas, 1892). This distinction has not taken root, while the distinction between length-fast and length-slow chalcedony (alternatively termed quartzine) is still in use. As far as lutecite is concerned, Heaney and Post (1992) and Heaney (1995) proposed to identify this length-slow chalcedony with moganite, although accepting the existence of length-slow quartz, or rather quartzine.

Nowadays, there is overall agreement in relation to the fact that the principal characteristic of chalcedony is its microcrystalline grain size and fibrous habit. According to these two features, chalcedony has been considered either a quartz variety with a different petrographic texture or a disordered mixture of microcrystalline fibrous quartz and moganite. Given that quartz and moganite are two polymorphs and thus two distinct phases, chalcedony would not properly be a mineralogical phase but rather a mineralogical assemblage. In the absence of moganite, the application of this definition may become critical if we do not consider that microcrystalline fibrous quartz is structurally different from ideal macrocrystalline α-quartz (Heaney *et al.*, 1994).

With respect to α-quartz, the main distinguishing features of chalcedony are represented by its lower refractive index and density. These properties are due to the numerous grain boundaries and the presence of (on average) ~1–2 wt.% water; the latter being both molecular water $(H_2O)_{mol}$ (entrapped mainly in fluid inclusions and open pores) and chemically bound hydroxyl $(H_2O)_{SiOH}$ (*i.e.* silanole), concentrated mainly within grain boundaries and defect sites (F1örke *et al.*, 1982; Miehe *et al.*, 1984; Schmidt *et al.*, 2013). The solubility of chalcedony is greater than that of quartz and less than that of cristobalite and amorphous silica (Pelto, 1956; Fournier and Rowe, 1966; Fournier, 1977, 1985; Walther and Helgeson, 1977). This feature is strictly dependent on the quartz:moganite ratio, *i.e.* the larger the moganite content, the greater the solubility of chalcedony (Heaney and Post, 1992).

In practice, the use of optical microscopy makes it possible to distinguish the length-fast phase, which is chalcedony *s.s.*, from the length-slow phase. The latter can be examined further by means of XRD or Raman spectroscopy, in order to distinguish length-slow moganite (previously lutecite) from length-slow quartz, *i.e.* quartzine.

3.2. Formation conditions of chalcedony

In sedimentary and low-temperature hydrothermal environments, near-surface conditions are generally described as the most favourable ones for chalcedony formation (see *e.g.* White and Corwin, 1961; Cady *et al.*, 1998).

There is no overall agreement regarding the temperature of deposition of chalcedony. Taking into account results from laboratory syntheses and from natural outcrops, the temperature of deposition ranges from <50ºC to 300ºC. Most laboratory syntheses are performed currently at temperatures >150ºC but this generally reflects the voluntary choice of decreasing the processing time (see Heaney, 1993 with examples and references therein). In natural materials, the temperature range varies between 25ºC and 180ºC, although generally being <100ºC (Fallick *et al.*, 1985; Harris, 1989; Saunders, 1990; Heaney, 1993). However, decompression and boiling conditions may lead to extreme supersaturation of silica with respect to quartz that, in turn, may induce the deposition of chalcedony at temperatures >200ºC (Fournier, 1985). With respect to pressure, Carr and Fyfe (1958) demonstrated how pressure constrains chalcedony formation to shallow depths.

Regarding precipitation of chalcedony, both direct precipitation from solution and transformation from an amorphous and viscous silica gel must be considered. The latter case was supported experimentally by laboratory syntheses – which obtained chalcedony using gels and opals (Oehler, 1976; Kastner, 1980) – and models (Wang and Merino, 1990). Some authors suggested recognizing a gel precursor with the occurrence of the following features: dehydration cracks, slump structures, preferential silica deposition on the bottoms of cavities rather than on the sides and tops (Fournier, 1985), bulbous voids often disrupting the wall-banding, fortification structures (Moxon, 1991) and crenulated shapes of some agates (Garlick and Jones, 1990).

A complete resizing of these observations was proposed by Heaney (1993) who (1) provided alternative explanations (*e.g.* pseudomorphism), (2) showed the rarity of certain features (*e.g.* liesegang banding) and (3) demonstrated the partiality of several results obtained through laboratory experiments (*e.g.* silica gels and non-silica solids). Heaney (1993) concluded that chalcedony precipitates from a non-viscous mother fluid and indicated the fossiliferous Formation of Hillsborough Bay (Tampa, Florida) as direct evidence for this interpretation. In this regard, it is worth underlining that an "opal phase" has been observed in non-fibrous microcrystalline quartz (Graetsch *et al.*, 1985) and its transformation into chalcedony seems to involve the dissolution of cristobalite instead of a solid–solid reaction (Mizutani, 1966; Stein and Kirkpatrick, 1976; Williams and Crerar, 1985).

From a diagenetic point of view, the most interesting conclusion reached by Heaney (1993) regards the role of the solution chemistry in deciding which polymorph will form: under conditions of equal pressure and temperature, chalcedony requires smaller concentrations of silica than cristobalite and larger than quartz.

The role of pH proved to be of critical importance in determining the spherulitic texture of chalcedony. Numerous studies demonstrated that the linearity of siloxane (Si–O–Si) chains is a function of low-alkaline pH and that Na^+ ions might inhibit branch formation, decreasing the number of bridging oxygens (Prassas *et al.*, 1982; Schaefer and Keefer, 1984; Schaefer, 1989).

At high temperatures (250–600ºC), chalcedony gradually loses silanole while molecular water is synthesized according to the reaction formulated by Schmidt *et al.* (2011, 2012b): $Si{-}OH + HO{-}Si \rightarrow Si{-}O{-}Si + H_2O$, further involving the closing of open pores. In length-slow chalcedony, the temperature of silanole loss is slightly lower (200ºC). In moganite, a temperature of ~100ºC seems to be supported by experimental data (Schmidt *et al.*, 2013), however, the experiments are never performed with pure moganite specimens (*i.e.* always moganite mixed with chalcedony). Moreover, unlike chalcedony, the water/silanole loss of moganite appears constant and regular, with no major events.

3.3. Moganite

The International Mineralogical Association's Commission on New Minerals and Mineral Names (CNMMN) approved moganite as a mineral species in 1999. It was recognized in the 70s by Flörke *et al.* (1976, 1984) and structurally characterized from the 80s (Miehe *et al.*, 1984). This phase derives its name from the Mogán formation on the island of Gran Canaria (Canary Islands); the formation consists of a sequence of pyroclastic and lava flows.

Moganite has monoclinic symmetry (Miehe *et al.*, 1988) with space group *I*2/*a* (Miehe and Graetsch, 1992). Its structure is described generally as alternate stacking of layers of right- and left-handed quartz, with a periodic twinning according to the Brazil-twin law at the unit-cell scale (Miehe and Graetsch, 1992; Graetsch *et al.*, 1994). A reversible transition from monoclinic α-moganite to orthorhombic β-moganite has been observed at temperatures > ~573 K, combined with the symmetry increasing from *I*2/*a* to *Imab* (Heaney and Post, 2001; Heaney *et al.*, 2007).

The water content is both molecular and silanole (Graetsch *et al.*, 1994). It can reach up to 3 wt.%, thus exceeding the chalcedony content of 1–2 wt.% (Graetsch *et al.*, 1985; Miehe and Graetsch, 1992). Moreover, both the silanole/molecular water ratio and the concentration of silanole groups are higher in moganite than in chalcedony, while molecular water contents are comparable or slightly lower (Flörke *et al.*, 1984; Miehe and Graetsch, 1992; Graetsch *et al.*, 1994; Schmidt *et al.*, 2013).

As for moganite solubility, Gislason *et al.* (1997) provided the value of 44 mg/kg (quartz solubility is 6 mg/kg), further determining that the dissolution rate of moganite is 7.4 times faster than that of quartz at pH 3.5 and 25ºC. The instability of moganite is regarded as being the most reliable explanation for its gradual decrease with the age and/or the alteration of the hosts, until its complete "disappearance".

As for the occurrence moganite, Heaney and Post (1992) demonstrated that this is a common mineral, being present in chalcedony, agate, chert and flint with percentages that range between 5 and 20 wt.% on average. The same authors detailed this estimation providing the following values: between <5 wt.% and >20 wt.% in both agate and chalcedony; between <5 wt.% and >75 wt.% in chert; and from 13 to 17 wt.% in flint. Heaney (1995) further distinguished evaporitic from non-evaporitic silica, respectively including 20–75 wt.% or 5–15 wt.% of moganite. Herdianita *et al.* (2000a,b) and Rodgers and Cressey (2001) found moganite levels of <13 vol.% in microcrystalline quartz-bearing sinters (between 20,000 and 200,000 y old) from the Taupo and the Coromandel Volcanic Zones of New Zealand. Some years later, Moxon and Rios (2004) indicated a value of 14 wt.% as the maximum moganite content in their agates.

Among archaeometric studies, Roman age gemstones from Vigna Barberini in Rome (Gliozzo *et al.*, 2011) showed variable moganite contents: 19–23 wt.% in two colourless chalcedonies, 0–35 wt.% in 13 orange carnelians, 12–14 wt.% in an onyx, 15–27 wt.% in three green Cr-bearing chalcedonies. Similarly, moganite contents ranged between 4 and 53 wt.% or between 6 and 16 wt.%, respectively, in carnelians and chert found in the Fezzan desert (Gliozzo *et al.*, 2014).

The general consideration that can be drawn from these data is that the wide variability of moganite contents are not visibly related to the variety (*i.e.* chalcedony, agate, chert, *etc.*) but rather to geological origin (host types and geographical location).

Another important aspect of moganite occurrence is that this phase can form in various environmental conditions and that its thermodynamic stability field is still uncertain. It can be argued that moganite is a strictly low-pressure crustal mineral, which can form in low-temperature evaporitic brines as well as in silica-rich hot waters (Heaney *et al.*, 2007). Heaney (1995) indicated that moganite can be used as a "valuable indicator for vanished evaporites", based on the frequent association of chalcedony with evaporitic regimes (*e.g.* Folk and Pittman, 1971). Moganite occurrence in the presence of hydrothermally altered basalt veins (Flörke *et al.*, 1982; Heaney and Post, 1992; Parthasarathy *et al.*, 2001), as well as with volcanic activity in general (Moxon and Ríos, 2004) has been shown repeatedly. Moreover, Parthasarathy *et al.* (2001) described moganite stability up to the laumontite zone of zeolite facies. The identification of moganite has also been the research topic in the Martian studies performed by Hardgrove and Rogers (2013).

As for dating, the first studies fixed ~100 Ma as being the maximum age of the host-rocks (*i.e.* Cretaceous Period; Heaney and Post, 1992). Rodgers and Cressey (2001) never found moganite in sinters younger than 20,000 y BP while it was present in rocks more than 40,000 and less than 200,000 y BP (Herdianita *et al.*, 2000a,b; Rodgers and Cressey, 2001). These authors further specified that, within this wide chronological range, moganite was rare or absent in most Tertiary sinters (*i.e.* from Paleocene to Pliocene). Moxon and Rios (2004) and Moxon and Reed (2006) showed that traces of moganite were present in agates older than 400 Ma. This limit in the Devonian period has been taken as the reference chronology now in use. Indeed, it is worth underlining that the chronologies provided by several authors are those of the host-rocks and there are some cases in which moganite may be secondary and, as a consequence, later.

3.4. Diagenetic transformations and selective growth of moganite

Heaney *et al.* (2007) described moganite as a "metastable transitory phase during silica diagenesis". Heaney (1995) further proposed a sequence of transformations with moganite as a follower of magadiite and a precursor of quartzine which, in turn, would have been a precursor of quartz:

Magadiite → (Kenyaite) → Moganite → Quartzine → Quartz

Many scholars have recognized moganite as the typical intermediate phase in the diagenesis of geothermal opal-A to quartz (Rodgers and Cressey, 2001; Rodgers and

Hampton, 2003; Hampton *et al.*, 2004). Herdianita *et al.*, (2000b) indicated the duration times for both the Opal-A → Opal-CT and/or Opal-C transformation (10,000–50,000 years; shorter in the presence of other components) and the quartz crystallization (20,000–50,000 years); however, the placement of moganite (detected in aged samples) within the sequence was not specified. Conversely, moganite (found in 20,000–200,000 years old sinters) and quartz were regarded as the resulting products of the maturation process of an opaline precursor by Rodgers and Cressey (2001):

$$\text{Opal-C} \rightarrow \text{Quartz} + \text{Moganite}$$

A few perplexities arise in relation to moganite transformation into chalcedony postulated by Moxon and Ríos (2004) and Moxon and Reed (2006).

As for selective growth, the reasons why moganite forms rather than quartz are not yet completely understood. Heaney (1995) provided two possible explanations: (1) structural affinities between moganite and its precursor (*i.e.* magadiite in that instance); and (2) the chemistry of the parent fluid. In the second case, Heaney and Post (1992) and Heaney (1995) suggested that alkaline and/or sulfatic fluids, possibly combined with ferric iron, were likely to control moganite precipitation. In this regard, Heany (1994, with related reference therein) showed that the transformation of Gran Canaria moganite to quartz was strongly promoted by ferric iron.

In summary, the diagenetic transformation of moganite depends on time, temperature and weathering and it progresses to the end-transformation into quartz, regardless of whether it crystallized directly or from an opaline precursor.

3.5. Moganite and quartz identification and quantification: a tool for the provenance issue in Archaeometry

The structural relationships between moganite and quartz have long created difficulties in discriminating these two phases by XRD; in fact, many of the major peaks of moganite overlie those of quartz (Fig. 3). However, the present state of the art is able to distinguish moganite from quartz and to quantify the respective percentages in weight by combining XRD with Rietveld refinement.

For quartz:moganite ratio determination, Raman spectroscopy is used increasingly in view of its ease and rapidity. Kigma and Hemley (1994) demonstrated that the moganite pattern is easily distinguishable from that of quartz, based on its intense peaks centred at 501, 220 and 129 cm^{-1} and less intense bands in the ranges 250–480, 650–850 and 1040–1210 cm^{-1} (Fig. 4a).

Götze *et al.* (1998) made a step forward demonstrating that the intensity ratios of the main symmetrical stretching-bending vibrations of α-quartz (465 cm^{-1}) and moganite (502 cm^{-1}) were indicative of the respective weight percentages of the phases. They further established that Raman measurements were not affected by the non-orientation or the non-preparation of the samples and that the resulting values for moganite contents were systematically higher than those obtained by XRD. Given that Raman spectroscopy was focused on an area 2.5 μm in diameter while powdered samples were used for XRD investigations, this shift was imputed to the different time of observation

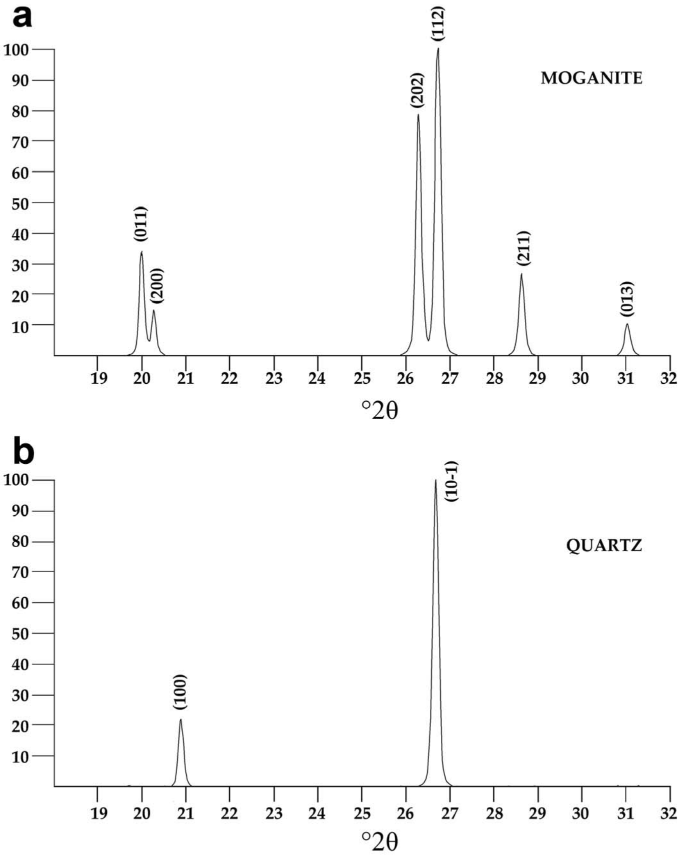

Figure 3. X-ray diffraction patterns (Cu-*K*α) of moganite and quartz (º2θ scale) from (a) Miehe and Graetsch (1992) and (b) Smith and Alexander (1963).

of these two techniques. Raman results were considered more significant than those obtained by XRD, the latter having greater difficulties in quantifying poorly crystalline phases. Schmidt *et al.* (2014) warned of spectral interferences resulting from silanol bands which can lead to an overestimation of moganite content. For this reason, they recommended heat-treatment in order to reduce the interferences.

Gliozzo *et al.* (2014) applied both XRD and Raman spectroscopy to the investigation of a collection of carnelians and cherts. The intercalibration was extremely satisfactory, clearly indicating that when experiments and data analysis are performed carefully both techniques yield reasonable assessment of the mineral-phase quantities.

Moreover, the utility of (thermal) infrared spectroscopy for the quantitative determination of quartz and moganite has also been demonstrated (Graetsch, 1994, *e.g.* fig. 9; Hardgrove and Rogers, 2013).

In geology, the quantification of the quartz:moganite ratio is becoming increasingly common (see above cited literature as well as Pop *et al.*, 2004) while it is still infrequent

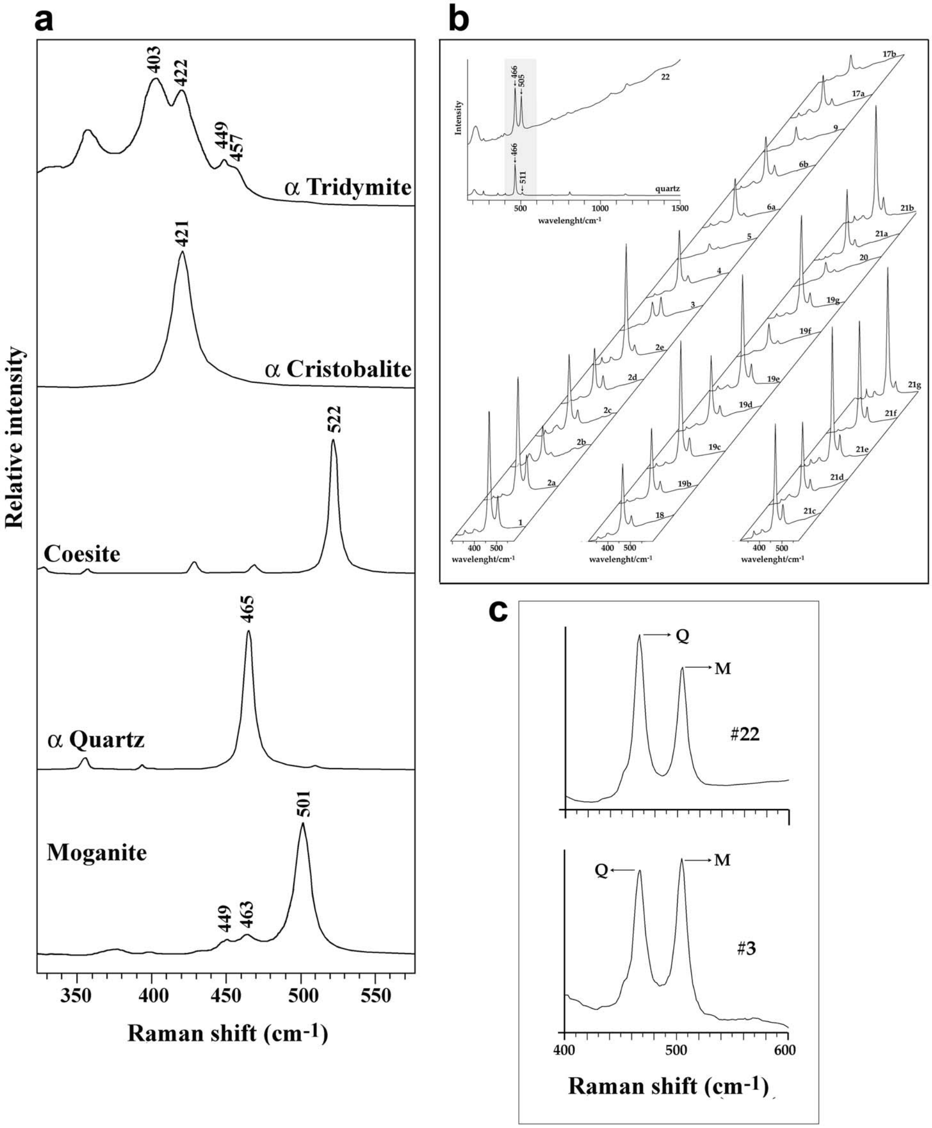

Figure 4. Raman spectroscopy. (a) Raman spectra of tridymite, cristobalite, coesite, quartz and moganite after Kigma and Hemley (1994). (b–c) The Raman spectra of 30 samples of carnelian and chert from the Fezzan desert; (c) the detailed view of two spectra where quartz and moganite contents are nearly equivalent.

in archaeometry, although it may represent a powerful tool for discrimination and, as a consequence, for provenance studies. There is very little information available on the topic (Pretola, 2001; Gliozzo *et al.*, 2011, 2014; Capél Ferron *et al.*, 2014; Gołyźniak *et* *al.*, 2016; Patrizi *et al.*, 2016; Prinsloo *et al.*, 2017; Wadley *et al.*, 2017; note that in some papers terminology and interpretations are not accurate) but this specific investigation, combined with bulk chemical data on major-, minor- and trace-element contents can support reasonable hypotheses on gemstone provenance. For instance, the results obtained on a collection of 16 carnelians and 15 cherts from the Fezzan desert by means of LA-ICP-MS, XRD and Raman spectroscopy (Fig. 4b–c) ruled out their importation from India and defined a reliable reference group for these materials, which were likely derived from a unique geological source (Gliozzo *et al.*, 2014).

Conversely, the exclusive application of Raman spectroscopy, especially when used merely for a phase determination, leads to such a partial characterization of the materials – even when non-destructive techniques are the only practicable ones – that it is no longer acceptable, except for a preliminary study aimed at research planning. A rapid overview of the principal applications of Raman spectroscopy in the field of archeo-gemmology is provided by Bersani and Lottici (2010, with references therein) while a review on the application of Raman spectroscopy in the wider field of gemmology is provided by Kiefert *et al.* (2012) and Kiefert and Karampelas (2011).

4. Agate

Agate is constituted mostly by chalcedony but it can also contain opal and macrocrystalline quartz as the final filling. It is characterized by multiple colours, typically distributed with a banded pattern. Many varieties are currently distinguished for commercial use based on their macroscopic characteristics (*e.g.* fire agate and Thunderegg; Fig. 5) and colour (*e.g.* blue lace agate) or area of origin (*e.g.* moss agate/mocha stone/Mokkastein from the ancient supply area of Mocha in Yemen, see Frondel, 1962 for further details on supply areas; Botswana agate, Laguna agate, *etc.*).

It can show the full range of colours (white, yellow, red, green and light blue) and, as clearly described by Graetsch (1994), can be of two types: wall-lining (concentric banding) or horizontally banded (Fig. 6). The former shows fibres radiating towards the centre of the geode, forming characteristic “parabolic fiber bundles”; conversely, in the horizontally layered agates, each layer may show “closely packed radiating spherulites” (Fig. 7).

The colours of agate are red, orange, brown, yellowish, purple, white, grey, green and, more rarely, blue. Agate with particularly intense colours are frequently dyed (*e.g.* Fig. 8), mainly by immersing a porous specimen in a coloured solution (*e.g.* cobalt nitrate for intense blue agate); however, many different kind of treatments are currently in use (see *e.g.* Scholz *et al.*, 2012 and Sindelar *et al.*, 2016, with references therein).

Given the enormous variety of rocks that goes under the name of agate, it is clear that the term does not indicate a well defined group of materials. Two main features should be required in order to classify a specimen as an agate: (1) it must be made primarily of chalcedony, or rather of fibrous quartz and variable amounts of moganite, and (2) it must show a banded pattern, otherwise it should be classified as chalcedony. As for feature 1, however, it is worth noting that an age- and weathering-dependent phase such as moganite can be absent.

Figure 5. A Thunderegg from Germany (Photo courtesy of Richard Nass).

Similarly to chalcedony, the origin of agate formation and its growth mechanism have long been debated without finding a single, widely accepted, model. Although Nacken provided the first reliable synthesis of chalcedony with a geode-like structure in 1948 (Nacken, 1948), the fact that nobody has yet been able to reproduce agate in a laboratory does not help.

It is difficult to generalize whether the entire sequence from amorphous silica to chalcedony (*e.g.* Moxon *et al.*, 2013) or the direct precipitation of chalcedony is involved in agate formation. These processes are closely tied to the surrounding conditions and there are still many unresolved problems in silica transportation, deposition and crystallization assessment. For instance, the self-organizational crystallization of agate postulated by Merino *et al.* (1995) and Wang and Merino (1995) involved a chemically controlled (*e.g.* silica saturation) self-organization of a non-crystalline precursor. Otherwise, in the model proposed by Heaney in 1993 (see also Frondel, 1978), a screw dislocation along the $[11\bar{2}0]$ direction should activate a spiral growth mechanism, which induces short-chain linear polymers to join *via* bridging silica monomers. Heaney and Davis (1995) explained banding in Iris agate

Figure 6. A specimen of agate from South Africa (author's personal photo collection).

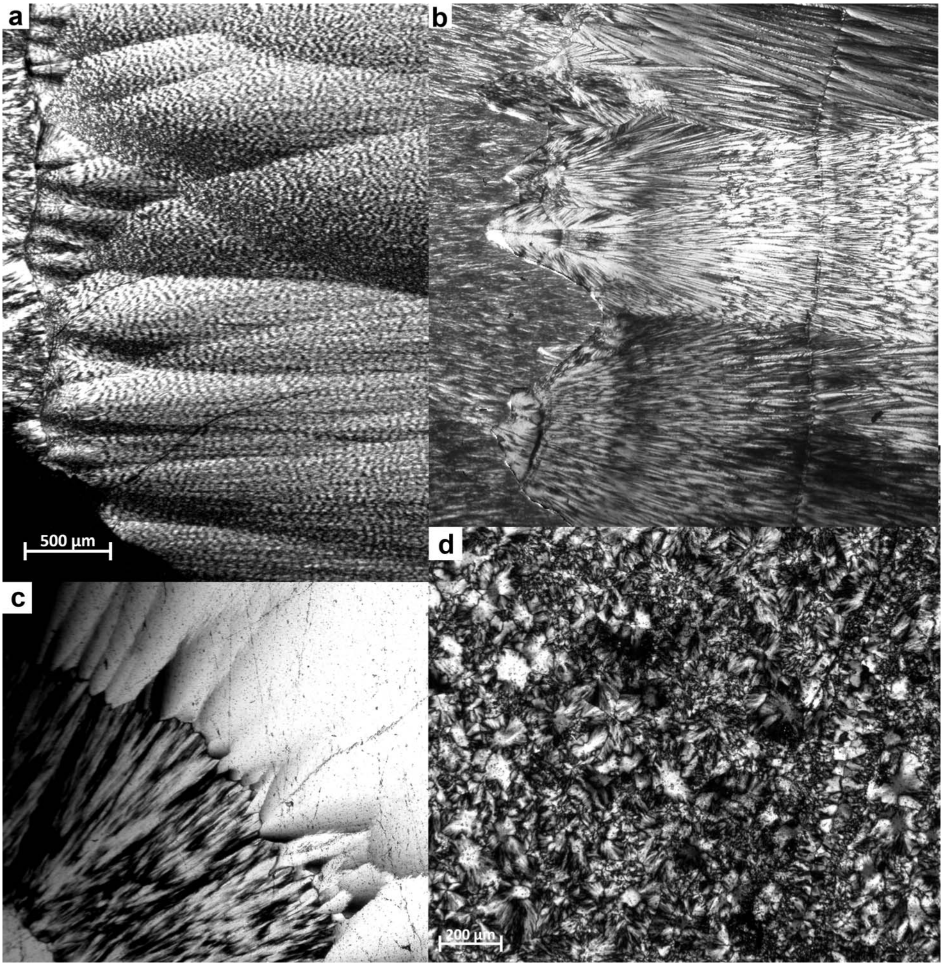

Figure 7. Agate at the optical microscopy scale (500 µm scale in a; 200 µm scale in b–d). (a–b) Length-fast fan-shaped chalcedony in a wall-lining agate. (c) Length-slow quartzine/moganite between length-fast chalcedony; and (d) zebraic chalcedony in a horizontally banded agate (author's personal photo collection).

with Ostwald-Liesegang crystallization cycles from silica-rich fluids. The Landmesser (1995, 1998) model proposed the following sequence: amorphous silica → cristobalite = tridymite → cristobalite → (±calcedony + moganite) → granular quartz. Lastly, Götze *et al.* (2016) investigated agates from Permian volcanic rocks of the Sub-Erzgebirge basin (Saxony, Germany) and explained their formation by "crystallization v*ia* an amorphous silica precursor under non-equilibrium conditions".

The banding phenomenon may represent alternating phases of activity and rest in the crystallization process. It can be influenced by the Fe oxide 'self-purification' process

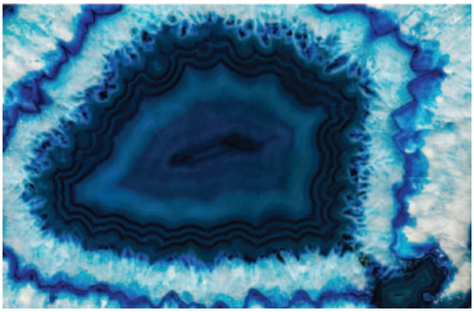

Figure 8. A treated (dyed) agate.

during crystallization (Götze *et al.*, 2009), and/or by Al^{3+} and Fe^{3+} substitutions for smaller Si^{4+} (Wang and Merino, 1990, 1995) and/or by textural and structural changes (fine-grained highly defective chalcedony and moganite/coarse-grained low-defect quartz; see Heaney and Davis, 1995; Götze *et al.*, 1998). French *et al.* (2003) postulated that bands form "as a result of discrete influxes of silica-rich fluid" and recognized a constant sequence within individual bands ("chalcedony-A (with amorphous silica and nano-crystalline quartz) → chalcedony-MQ (with microcrystalline quartz) → quartz") which is proposed as "a viable model for the growth of chalcedony in agates". Furthermore, horizontal banding is generally assumed to be gravity-controlled (Moxon and Reed, 2006).

One of the few points on which there seems to exist a broader agreement concerns the formation temperature, which is estimated to be <100ºC (Heaney, 1993) in basic igneous rocks (Fallick *et al.*, 1985; Saunders, 1990); however, the higher temperatures (>400ºC) proposed for agates in volcanic environments (Moxon, 1996 with references therein) have been supported experimentally by chalcedony reproductions.

As for the estimation of the age of agate formation, Moxon (2017) investigated mobile and total water content of 60 agates (from 23 to 2717 Ma) in relation to host-rock age and it turned out that water contents showed age-related trends in agates up to ~60 Ma. Furthermore, it was established that Brazilian (135 Ma) and New Zealand (89 Ma) agates formed much later than their host-rock.

Lastly, the "unusually high uranium content" in the agates from Germany, Poland, Mexico and USA have been investigated by Götze *et al.* (2015).

4.1. Pliny on agate: description and provenance

Pliny was the first to list the many terms used for describing agate (*N.H.* 37, 139): "*iaspachates*" (jasper-agate), "*cerachates*" (wax-agate), "*smaragdachates*" (emerald-agate), "*haemachates*" (bloodagate), "*leucachates*" (white agate), "*dendrachates*" (dendritic agate = moss/mocha agate), "*antachates*" (not translatable with certainty, text maybe corrupted), "*corallachates*" (coral agate, "sprinkled with golden particles"), and "*sacra*" (in reference to its power to counteract the bites of spiders and scorpions).

Three paragraphs (*N.H.* 37, 136-138) were dedicated to the Iris agate (= moss agate). According to the author, this variety (a) corresponded to rock crystal – the reason why it was also called '*radicem crystalli*" (root of crystal), (b) had hexagonal faces, like the rock crystal, (c) scattered the light shining upon it, and (d) projected lighting at the same time to the objects around (*N.H.* 37, 137). Also according to Pliny and his sources, there would also be another rainbow stone in Persia called '*Iritis*' and other gems of similar appearance but black and white in colour, called '*leros*' (*N.H.* 37, 138).

Pliny further supplemented his description of agates with information gathered by the science of the Magi, although the latter were frequently attacked in tones of scorn and contempt (*N.H.* 28, 6-7, 228-229: 30, 17-19, 95). Judged extravagant, frivolous and patently irrational, they were often defined as false and impostors but their beliefs about agates were still reported. In fact, Pliny (*N.H.* 37, 142) described the ability of agates to keep scorpions away (when the gemstone resembled a lion's skin), to avert storms and waterspouts, to stop the course of rivers (when linked to the hairs of the mane of a lion), or even to make athletes invincible (a particular type of monochrome agate). In addition, Pliny reported the test to run in order to verify that the stones were actually effective: the stone should have been immersed for a least two hours in a pot of boiling oil, together with unspecified pigments. At the end of the test, all the pigments would have to have acquired a vermilion colour.

As for provenance, Pliny reported that agate was discovered first in Sicily, near the homonymous river. The most likely identification of this ancient river *Achates* is with the current River Acate-Dirillo. This river comes from the Iblei mountains, runs by the village of Acate, flows near Gela and along its course of 54 km assumes different names, among which is Acate. A further identification with the modern "Carabi (Canatello)" river, "not far from Giuliana" was proposed by Eichholz (1962) but it is difficult to find a correspondence between these toponyms and the actual geography.

Still, according to what Pliny says, Sicily was only one of the many supply areas of this gemstone which enjoyed great esteem in the past but no longer had a great value in his time (*N.H.* 37, 139). Agates with the appearance of rivers, woods and livestock (see for instance the *murrina vasa* in Del Bufalo, 2016) were arriving from India and were used to make *paterae* (*i.e*. libation bowls), figurines, horse-trappings and small mortars used by pharmacists. Moreover, it was said that, among other things, agate possessed an important property to dispel thirst by holding it in the mouth (*N.H.* 37, 140).

The "coral agate" was characterized by golden particles like those of lapis lazuli and was used extensively in Crete; however, the Plinian text does not clarify whether Crete was also the place of extraction (*N.H.* 37, 139); moreover, given the wide use of agate for the seals in Minoan Crete (Walters, 1897; Boardman, 1970; Spier, 1992), it is likely that this information resulted from a suggestion.

The Phrygian (modern Turkey), Egyptian (Thebes) and Cypriot agates were also mentioned, specifying that the first contained no green hues, the second did not show red and white veins, while the third had transparent glassy portions (*N.H.* 37, 141). Other supply areas were the Trachis region (near Mount Oeta, place of Heracles' death), Mount Parnassus, Lesbos, Rhodes and the Messenia district (southwestern Peloponnese); the last-named providing agates with flower-like patterns (*N.H.* 37, 141). As for the provenance of Iris agate, Pliny reported that it was excavated on an island in the Red Sea, 60 Roman miles (~88 km) from the city of Berenice (*N.H.* 37, 136). It is perhaps no coincidence that, at approximately the same distance (82 km as the crow flies), there is the volcanic island of Zabargad (Saint John's island), which was the supply area of the best peridot (Wilson, 1976).

The localization of the toponyms mentioned by Pliny is shown in Fig. 9.

4.2. Past and current supply areas

Agate occurrence is generally related to volcanic environments, especially to basaltic, andesitic, dacitic and rhyolitic hosts (Götze *et al.*, 2009); conversely, agates are rarer in sedimentary and metamorphic hosts (Clark, 2002; Moxon and Reed, 2006; Moxon *et al.*, 2006, 2007).

In Europe, one of the larger deposits was that at Idar-Oberstein (Germany; Fig. 9), where agate was extracted and worked on an industrial scale until the 19th century (Frazier *et al.*, 1998–1999). When the deposit was almost completely exhausted, agate was imported from the Brazil mines of Rio Grande do Sul which were discovered by Idar-Oberstein migrants and shipped as ballast. The exploitation of the Idar-Oberstein deposit in an earlier period has not yet been demonstrated, although it is very likely. The area is still the object of amateur research and the seat of the important Edelstein museum where agates from all over the world are collected (Fig. 10).

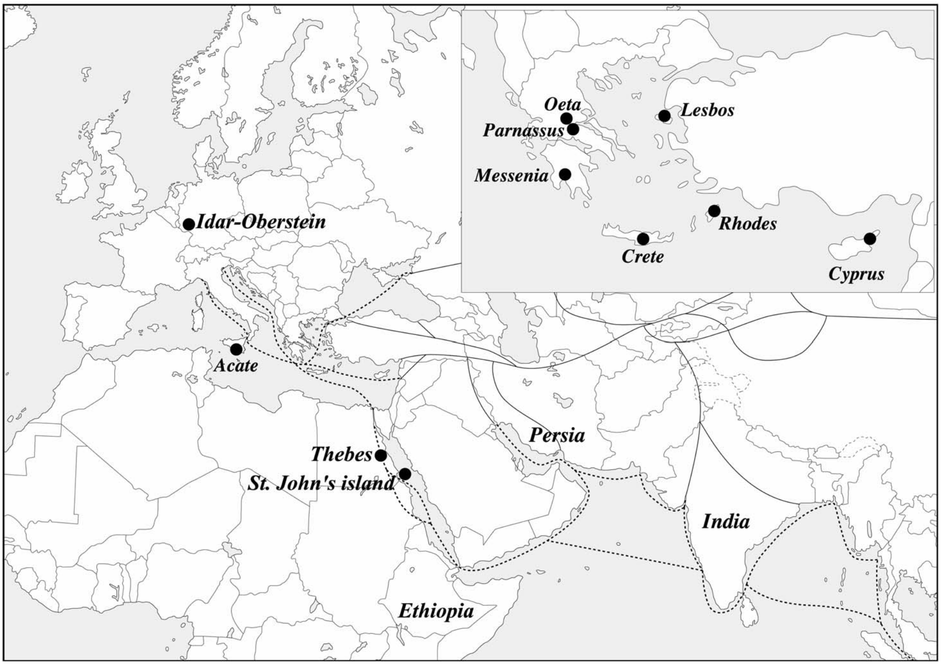

Figure 9. From the *Naturalis Historia* by Pliny the Elder: the distribution of *achates*. The silk road and the principal maritime routes are shown, as well as the localization of Idar-Oberstein.

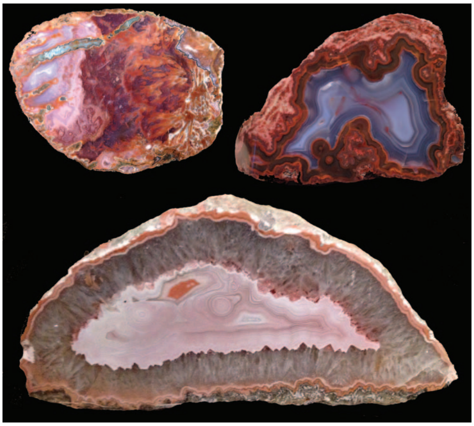

Figure 10. Some of the marvellous agates preserved at the Idar-Oberstein Museum. The upper two are from Argentina while the other is from Freisen, a locality close to the town (author's personal photo collection).

The major supply sources for the modern market are Brazil (see Scholz *et al.*, 2012 for further details), Madagascar, Argentina, Uruguay, Mexico, Poland (for those from Płóczki Górne see Dumańska-Słowik *et al.*, 2017), Botswana, India (Deccan), Australia and the United States (Oregon, Arizona, Montana, Wyoming, South Dakota and Michigan).

Recent interest has arisen also in relation to both Moroccan agates (Natkaniec-Nowak, 2016) and Serbian deposits. The latter are poorly known but rich in opal, carnelian, bluish chalcedony, chrysoprase, jasper, rock crystal, amethyst and many other precious hard stones (Miladinović *et al.*, 2016).

Lastly, it is perhaps worth remembering that coral and fossilized wood are frequently termed as "agatized" when silicified.

4.3. Agate provenance in archaeometry and information gained from the geological literature

Excluding chert and flint, agate has received the widest attention in archaeometric studies. In fact, a total of 183 samples (including carnelians), found in Afghanistan, Cambodia, India, Iran, Italy, Lybia, South Africa and Thailand were investigated geochemically. Among these studies, that performed by Law *et al.* (2012) is of outstanding importance because it demonstrated how different sources could be differentiated, providing reasonable discrimination for the three agate deposits in India as well as with respect to eastern Iranian and Thai agates (Fig. 11). Although lacking in archaeometric analyses, the study conducted by Kenoyer *et al.* (1994) is of further interest as it includes the recognition of numerous ancient agate working sites in India.

The number of investigated geological materials is smaller but with a wider geographic distribution. Excluding materials from Japan as well as oceanic materials, geochemical analyses are available for at least 171 examples from: Brazil, Canada, the Czech Republic, Germany, India, Iran, Lesotho, Mexico, Namibia, Poland, Thailand, Turkey, the United Kingdom and the USA (see Appendix 2).

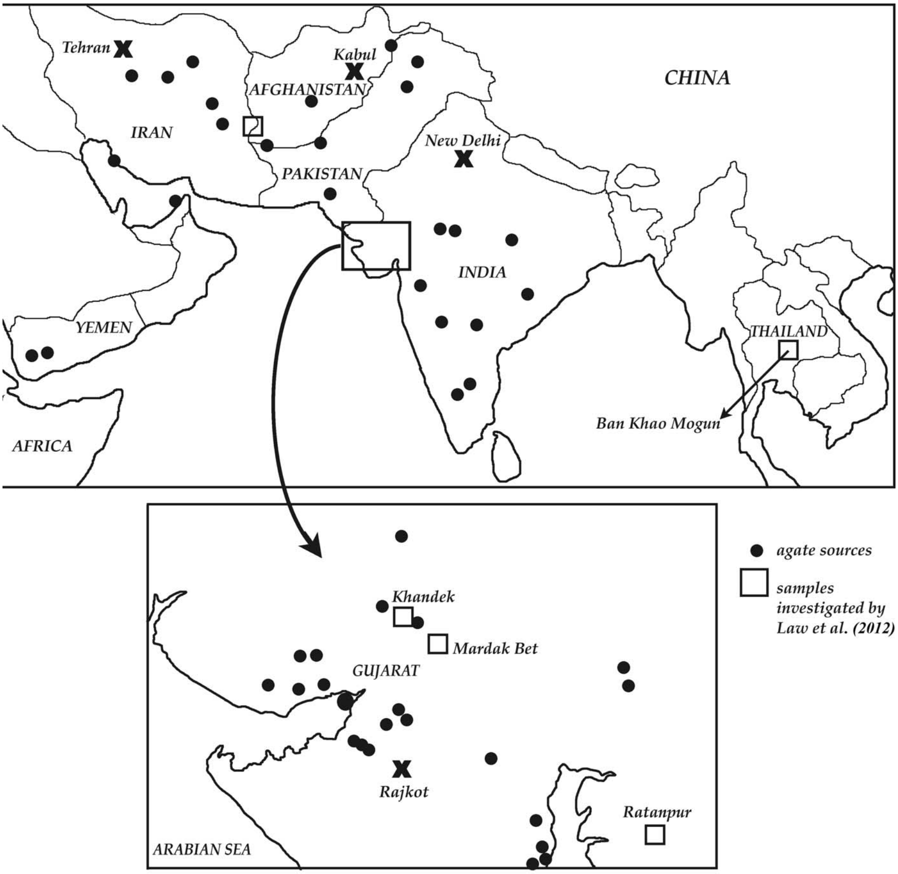

Figure 11. Agate – source distribution in Yemen, Iran, Afghanistan, Pakistan, India and Thailand from Law *et al.* (2012). The localization of samples investigated by Law *et al*. (2012).

Given that quantifications are provided for agate and carnelian together, please also see Section 5.4. on "Carnelian provenance in archaeometry and the information gained from geological literature".

5. Chalcedony varieties

Similarly to the scheme adopted previously for agate, the following sections will provide information about:

(1) the fundamental characteristics of chalcedony varieties from a mineralogical point of view, in order to establish the basic criteria to distinguish them;

(2) the information passed on by Pliny, especially with regard to the origin of these gemstones, in order to assess the knowledge and beliefs about these minerals and the supply areas known at the time;

(3) today's main extractive areas and deposits, in order to gather additional information on the availability of these gemstones:

(4) the archaeometric studies performed on archaeological gemstones, in order to obtain an insight into the current state of the art on these topics.

5.1. Red and orange chalcedony: carnelian and sard

The term carnelian (*corniola* in Italian, *cornaline* in French, *karneol* in German) is applied to the orange-red translucent variety (Fig. 12) while the term 'sard' (*sarda* in Italian, *sardoine* in French, σάρδιον in ancient Greek) is used for the dark-orange to brown varieties. These chalcedony varieties consist of a mixture of microcrystalline quartz and moganite and owe their colour to small hydrous iron oxide inclusions (Fritsch and Rossman, 1988).

Carnelian can be obtained by heat-treating agate, in order to enhance the colouring effect of hematite. The same result can be obtained using an iron nitrate solution or other appropriate dyes. Usually, dyed carnelians show a striped pattern against the light, while untreated carnelian has a cloudy appearance.

Both carnelians and sards have always functioned as decoration and status markers. The Egyptian civilization used carnelian for the manufacture of scarabs and beetle-shaped amulets, symbols of resurrection and the human soul's endurance. In more recent times, this tradition was passed down by Phoenicians, Greeks, Romans and Etruscans, as well as by the first Christian communities, for its ideological connection with the resurrection. During Roman times, carnelian and sard were used mainly to make engraved gems (*N.H.* 37, 105) for luxury items, with an apotropaic finality or lucky charms. Hot wax does not stick to these gemstones and this property has determined their further use as seal rings since the Assyrian civilization.

5.2. Pliny on carnelian, sard, *carbunculus* and *charchedonia*: description and provenance

As frequently happens with Plinian text, the description of carnelians and sards suggests that different types of gems were grouped under one name. It seems, in fact,

Figure 12. Carnelian and quartz from the territory of Idar-Oberstein, Germany (Personal photo collection).

that the same material was unknowingly named in four different ways: carnelian, sard, *carbunculus* and *charchedon(ia)*.

According to Pliny, the colour and the aspect of carnelians and sards were used in order to distinguish their provenance (*N.H.* 37, 105-107). Greek and Egyptian sards were characterized by being backed with gold foil, while those from India were of three different varieties: a red variety, a '*pionia*' variety (so-called for its greasy lustre) and a third variety backed with silver foil. The honey- and the earthenware-coloured varieties were so despised by Pliny that he does not even say where they came from.

Pliny asserted that sard was first discovered at *Sardis*, identified as Σάρδεις in Lydia (modern Sart) and not as Σαρδώ (modern Sardegna) as had been hypothesized. Onsite investigations have never been performed and modern researchers presume that the word *Sardis* has nothing to do with that town. In fact, the term should derive from "sered", a Persian word meaning yellowish-red.

However, Pliny added that the most valuable specimens were found near Babylon; moreover, he mentioned several other sources such as Paros and Assos (modern Behramkal, Turkey), India, Arabia, Epirus and Egypt, as well as exhausted sources in Persia (*N.H.* 37, 105-106).

According to Eichholz (1962), India should be the true source of those quoted by Pliny as being from Persia and Babylon. However, the summary traced by Charpentier *et al*. (2017) indicates that many other possibilities were absolutely reliable. In fact, the first productions of carnelian and agate beads emerged in Baluchistan (eight millennia BCE) and in northern Mesopotamia (a millennium later; Inizan, 1995) and became frequent in lower Mesopotamia (Ubaid culture, fifth millennium). Given that geological sources have not been identified along the Arabian coast, Inizan (1995, 1999) suggested that Mesopotamian beads were traded by the coastal Neolithic societies of the Gulf while Crawford (1998) proposed an Iranian origin. During the Middle Neolithic period, hard-stone beads made their appearance in Arabia (Inizan, 2007) while the earlier occurrences of carnelian beads in southern Arabia date back to the second millennium BCE (Inizan, 2007; Crassard, 2008). Furthermore, between the sixth and the fourth millennia, carnelian and agate from the Jebel al-Ma'taradh (Emirate of Ra's al-Khaimah) were surely exploited to make beads (Charpentier *et al*., 2017).

In this regard, it is worth discussing the eventual correspondence of carnelians/sards with the incombustible *carbunculus* gemstone cited by Pliny (*N.H.* 37, 92-97, 103-104), but more frequently referred to as a pyrope garnet (see for instance http://www.mindat.org/gm/28904).

Pliny stated clearly that there were several types of *carbunculi*. The first variety from India was flawed, with a parched lustre and rather opaque but it allowed the creation of large vessels and showed brighter colours than the second variety.

The latter is described twice in *Liber* 37th. The first mention appears in chapters 92-97 and presents these *carbunculi* as gemstones linked to the Garamantes people, who were also called *Charchedonios* (*i.e.* Carthaginian), in honour of the greatness of Carthage. In fact, according to *Eusebius*, the Tyrians or Phoenicians *Charchedon* and

Zorus founded Carthage thirty years before the destruction of Troy. In Rome, Garamantian carbuncles were known as "Carthaginian stones" possibly because Roman traders initially accessed these gemstones *via* Carthaginian traders (Gliozzo *et al.*, 2014). Still in this section of his book, Pliny lingered on the description of this variety, also reporting the opinion of his ancient colleagues *Callistratus* and *Archelaus*. The information gathered described the Garamantic *carbunculi* as small gems, with an overall dark appearance, tending to a violet hue in the shade or to a fire-red hue in the open air. They also sparkled if directed towards the sun, and were able to melt wax in the dark when used as signets. The further notation on the asterism of male *carbunculi* can be interpreted readily as implying that among the red stones called *carbunculi*, rubies were also included. The second mention appears in chapter 104 where Pliny insists on the African origin of *charchedonia*. He specified that these stones originated in the territory of the Nasamones and skeptically added that local people thought that they were formed by rains of divine origin. Similarly, Strabo indicated the Saharan mountains as the land from where the "Carthaginian stones" were brought (*Geography*, 17.3.11; 17.3.19), thus supporting the Libyan origin of the *charchedon*.

If, on the one hand, the ancient literary sources seem to indicate decisively the Libyan Sahara as a supply area for the *charchedon*, on the other hand we have no tools to further limit the possible areas of extraction. The mention of *Mons Gyri* as the source location in the territory of the Garamantes (Pliny, *NH* 5.37) does not find direct correspondence with modern toponymy. In this regard, the volcanic area of the Jabal Bin Ghanima (in the basalt province of al-Haruj), the Tibesti mountains or the plateau/mountains to the north of the Wadi ash-Shati may be potential source areas (Gliozzo *et al.*, 2014).

Another interesting aspect seems to be the confirmation that the Garamantes were particularly active in the gemstone market, not only for *carbunculus* but also for *sandastros* (also called Garamantic stone; see Pliny *N.H.* 37, 100-102). On reasonable grounds, therefore, this information should be interpreted as a very important provenance indication.

Going back to the description of *carbunculus* varieties provided by Pliny, the third one was of Ethiopian origin and characterized by a greasy appearance without any lustre (*N.H.* 37, 92).

The fourth variety was named *Alabanda* and was a darker and rougher variety found at *Orthosia* but treated at *Alabanda* (both sites were located in *Caria*, *i.e.* western Anatolia). The correspondence with almandine – which takes its name from the city of Alabanda – is absolutely clear in this case.

The fifth variety – the *lychnis* – was also supplied in Caria and the neighbouring regions (*N.H.* 37, 103). It was characterized by lamps lit with kindling wood and it was sometimes named 'mild carbuncle' when resembling the so-called 'Flower of Jove' (*i.e. Lychnis flos-jovis*, a flowering plant with pink flowers of the *Caryophyllaceaea* family; please note that in the same family of the *Caryophyllaceaea* is also included the red *Lychnis Chalcedonica*).

Among the varieties of *carbunculi* not affected by fire, Pliny mentioned that from *Miletus*, while *Theophrastos* quoted *Orchomenos* in Arcadia (dark variety used for mirror-making), Chios, Troezen (in Argolis), Corinth and Marseille as additional areas of discovery. *Lucius Cornelius Bocchus* (another Lusitanian colleague of Pliny) further wrote about how they were extracted with great difficulty near Lisbon (*N.H.* 37, 96-97).

Among other ancient authors, further information about these gems has been handed down by *Teophrastos* and the Greek epigrammatist poet *Posidippus* (Pella, *ca.* 310−240 BCE). The former distinguished a female and a male variety which could correspond to the distinction between carnelian and sard (*Lap.* 8, 23, 30). Pliny faithfully reported this belief (*N.H.* 37, 106), adding further that male and female gemstones could be distinguished based on their brighter or more opaque lustre, respectively, and, among the former, the 'stones of Syrtis' (*syrtitas*) were particularly appreciated for their red (core) and purple-amethyst (edges) bichromy (*N.H.* 37, 93).

This gender aspect was of particular importance especially when using crystals for therapeutic reasons; in fact, it was believed that their differential use had specific properties, in close analogy with the concept of yin and yang in Chinese philosophy.

Posidippus wrote about a very bright Sard, of at least a 66 cm side (if squared) or diameter (if circular), that excelled Indian rubies and bore the engraved image of Darius and his chariot (I 36- II 2; see the comments made by Casanova, 2004).

Lastly, Pliny provides further information on: (1) treatments in vinegar (14 days immersion) to make the gemstone brighter and (2) numerous counterfeits in glass which could be exposed through the use of grindstones and scales.

The locations of the toponyms mentioned by Pliny are shown in Fig. 13.

5.3. Past and current supply areas

The Indian deposits were the largest and their exploitation probably predates the Harappan period (see *e.g.* Allchin, 1979; Kenoyer *et al.*, 1994). They were not the only ones, however, because traces of processing have been found in Indonesia, West Java (Garut, Bungbulang mountains), East Sumatra (Kalienda, Lamphung region) and central Thailand (Lopburi area) (Bellina, 2003). In the last-named areas (Fig. 14), production centres and bead distribution between the last centuries BCE and the first millennium CE were studied by Bellina (2003).This author claimed that multiple Asian sources must have been exploited, therefore, an exclusive import from India would have been unlikely.

Recently, research into Fezzan (Libya) carnelians and cherts demonstrated for the first time that carnelian could have been of Saharan provenance (Gliozzo *et al.*, 2014). Similarly, the study conducted by De Waele and Haerinck (2006), helped to characterize numerous etched beads from northeast and southeast Arabia, in relation to a wide carnelian trade, possibly involving numerous source areas in the Deccan Plateau, Iran (Ratanpur in the Rajpipla, Shahr-i Sokhta in the Helmand Basin and on the Bushehr peninsula; see Whitehouse, 1975), Arabian Peninsula (al-Ghail, ~40 km south of Ras al-Khaimah, UAE), Yemen and western Saudi Arabia (references in De Waele and Haerinck, 2006).

Modern supply was concentrated mainly in India, before being flanked and partially supplanted by Brazil, USA, Sri Lanka and Uruguay. Among the numerous supply areas

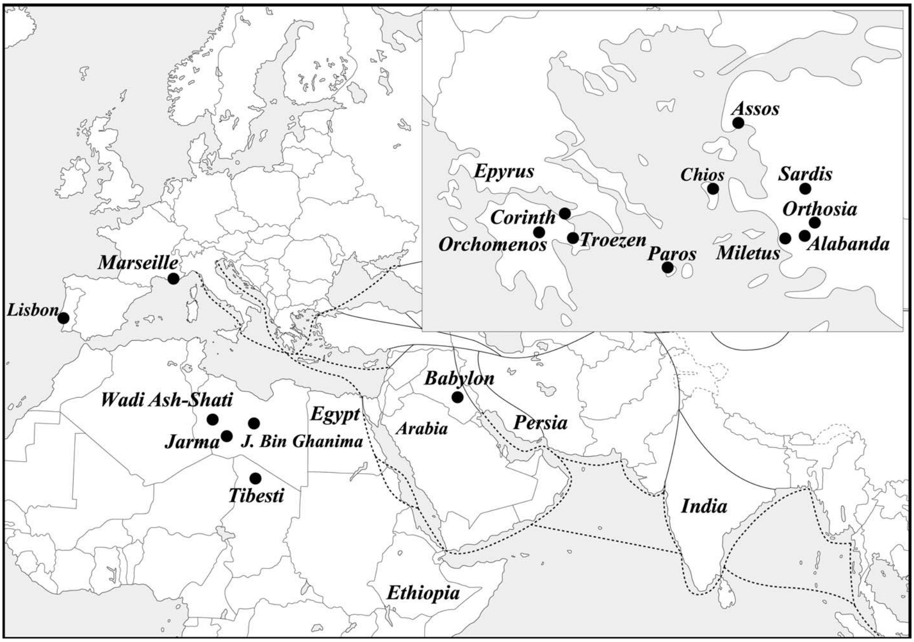

Figure 13. From the *Naturalis Historia* by Pliny the Elder: the distribution of carnelians. The silk road and the principal maritime routes are shown.

in the United States, Frondel (1962) mentioned Specimen Ridge and Amethyst Mountain in the Yellowstone National Part (Wyoming), Yellowstone River (Montana), Chehalis (Washington), Colorado Springs (Colorado), Fairburn (South Davota), Isle Royale (Michigan), Flint Ridge (Ohio) and other unspecified localities in Oregon.

5.4. Carnelian provenance in archaeometry and information gained from the geological literature

The trade in carnelian beads has been studied for a long time with the objective of tracing the interactions between different cultures and geographic areas (see Kenoyer, 2008; Kenoyer *et al.*, 2013 with references therein). Use-wear analyses and technological (/ethnographic) studies have invaded the archaeometric literature (*e.g.* Chevalier *et al.*, 1982; Gorelick and Gwinnett, 1990; Inizan and Tixier, 2000; Roux, 2000; Rosenfeld and Dvorachek, 2003; Kenoyer, 2005; Groman-Yaroslavski and Bar-Yosef Mayer, 2015), while provenance studies were virtually neglected. A few geochemical studies are currently available on archaeological carnelians from Cambodia, India, Nigeria, Sri Lanka, Thailand, Italy and Libya:

- Iron Age carnelian and agate beads from Cambodia and Thailand, investigated by Carter and Dussubieux (2016);
- Carnelians from modern mines and ancient manufacturing sites in India (Gujarat), Nigeria and Libya, investigated by Insoll *et al.* (2004), using UV-LA-ICP-MS;

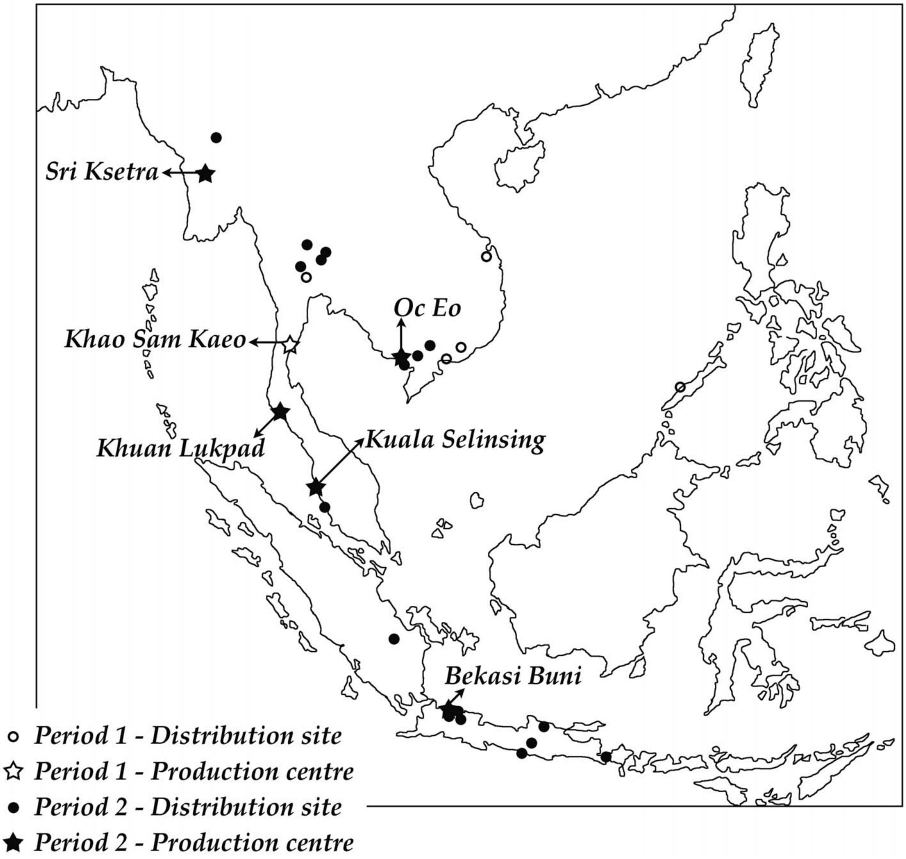

Figure 14. Agate and carnelian – Production centres and bead distribution between the last centuries BCE (Period I) and the first millennium CE (Period II) reconstructed by Bellina (2003).

- Carnelians from several sites in India, Sri Lanka and Thailand, investigated by Theunissen *et al.*, (2000), using PIXE/PIGME;
- Republican to 7th century AD carnelians from the archaeological site of Crypta Balbi (Rome, Italy), investigated by Andreozzi *et al.* (1996);
- 1st to 2nd century AD carnelians (11 samples) from the archaeological site of Vigna Barberini (Rome, Italy), investigated by Gliozzo *et al.* (2011), using XRD and PIXE;
- 4th century BCE to 4th century AD carnelians (16 samples) from the Fezzan region (Libya), investigated by Gliozzo *et al.* (2014), using XRD, Raman microspectroscopy and LA-ICP-MS.

Other studies only supply information about the discovery of carnelians, provide a very preliminary characterization of a few samples (Behar *et al.*, 2016) or include a detailed mineralogical characterization, but without geochemical measurements (*e.g.* Anghel *et al.*, 2016, among others cited above).

Geological literature on carnelians is also extremely rare. Two carnelians from Coşava (Banat, Romania) were investigated using LA-ICP-MS by Schmidt *et al.* (2012a). Geological sources for agate and carnelian from Thailand, Iran and India have been investigated by Carter and Dussubieux (2016).

Lastly, it is worth specifying that, in the literature, the terms agate and carnelian are often used interchangeably; therefore, this paragraph should be consulted together with a previous one (Section 4.3. Agate provenance in archaeometry and information gained from the geological literature) and quantifications for both are presented together in Appendix 2.

5.5. Black and brown chalcedony: onyx and sardonyx

Onyx and sardonyx are banded chalcedony, or rather agates, which differ only in their black and white or brown and white colourations, respectively. In both cases, however, onyx and sardonyx may indicate chalcedonies where only the black or the brown portions are visible. This is the case for ‘nicolo’ (or ‘niccolo’) onyx, which probably corresponded to the Plinian *Aegyptilla* (*i.e.* little Egyptian stone; *N.H.* 37, 148), characterized by a black ground and an upper layer of blue.

The colours may be due to Mn-oxide or Fe-oxide inclusions (Indian and South African agates), bituminous organic substances (Brazilian agates) or carbonaceous materials incorporated in the SiO_2 matrix during formation (agates from Mali; see Götze *et al.*, 2012 with references therein).

The colouration can be induced artificially by the staining process, *i.e.* immersing an uncoloured chalcedony in an aqueous solution saturated with sugar, honey or olive oil. The organic substances will penetrate the porous silica and will undergo dehydration and oxidation reactions when heated in a sulfuric acid solution.The colour obtained will not be stable over time and it will fade. Among other ‘gemstone simulants and enhancements’, the onyx/sardonyx treatment is explained clearly by Whalley (2012): “the material is first boiled in a solution of sugar ($C_{12}H_{22}O_{11}$); it is then heated or soaked in concentrated sulphuric acid (H_2SO_4) which reacts with the sugar to release carbon, thus producing a black or brown body colour.”

Although it was widely used for making jewellery (especially cameos, like the ‘Great Cameo of France’ or the “Apotheosis of Augustus”), cups, statuettes and other decorative items, Pliny briefly lingers on the description of onyx, without being particularly fascinated by it (*N.H.* 37, 90-91). He refers to the information received by his colleagues *Sudines*, *Zenothemis* and *Sotacus* about the Indian and Arabian onyx. The Arabian onyx is described as a black stone with white bands, closest to what we now refer to as onyx. Conversely, the Indian onyx was thought to have red and violet streaks, similar to those of the *carbunculus*. Apart from India and Arabia, the association of the *Aegyptilla* with the ‘nicolo’, should include Egypt among the ancient suppliers.

Modern supply areas are concentrated mainly in Brazil, Madagascar and Uruguay. However, the rarity of both onyx and sardonyx has prompted many manufacturers to produce it artificially.

To the best of my knowledge, there is no geochemical research on archaeological materials.

5.6. Green chalcedony: chrysoprase, Cr-chalcedony, "gem silica" or "chrysocolla chalcedony" and heliotrope

Chrysoprase (χρυσός = gold, πράσινον = leek) is characterized by an apple green hue (Fig. 15) caused by Ni-bearing inclusions rather than by substitutional Ni in the silica (Rossman, 1994 with references therein). NiO can reach up to 5.1% but it is not clear if it is always present as bunsenite (cubic NiO) or in other forms (Hyršl, 1999) such as layered Ni-rich silicates. In fact, Barsanov and Yakovleva (1981; quoted by Rossman, 1994) provided evidence of bunsenite, while a Ni-bearing phyllosilicate was found in chrysoprases from Australia, Poland and Kazakhstan by Nagase *et al.* (1997). Other authors (*e.g.* Sachanbiński *et al.*, 2001) found Ni-Mg silicate aggregate, such as garnierite (generic term, variously used as a synonym of falcondoite and/or népouite) or Ni-rich kerolite and pimelite (*i.e.* a Ni-bearing clay mineral not approved by the IMA). Furthermore, Graetsch (2011) demonstrated that the green colour of Tanzanian chrysoprase (Shigley *et al.*, 2009) was due to 0.47 wt.% of gaspeite (hexagonal nickel carbonate, $(Ni,Fe,Mg)CO_3$) while Čermáková *et al.* (2017) claimed that the presence of "pimelite" was responsible for the green colouration of the Szklary chrysoprase.

In any case, chrysoprase can be considered to be the corresponding chalcedony variety of the leek-green quartz variety called prase (quartz + chlorite); however, this latter term does not seem, at present, to be used to describe a single varietal name and it can be used for a variety of green opal as well (Shigley *et al.*, 2009). In addition to chromophores, chrysoprase can also include both tridymite and cristobalite.

Cr-chalcedony has a typical emerald green colour which is due to Cr inclusions, although minor quantities of nickel can be present as well. It is sometimes called

Figure 15. On the left, a chrysoprase from Poland (Photo by Xth-Floor – Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=15062186); on the right prasiolite crystals from Torre di Rio at Rio Marina, Elba Island, Italy (Photo by Didier Descouens – Own work, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=7853444)

matauralites or mtorolite because some specimens have been found near Mtoroshanga in Zimbabwe. The presence of Cr means this variety of chalcedony approaches the quartz variety called aventurine, although with a different source of colour. Moreover, it is also possible to add that fuchsite-bearing quartzite may correspond to the Plynian *sandastros* mentioned by Pliny (*N.H.* 37, 100-102).

Based on colouring agents (Ni for chrysoprase, Cr for Cr-chalcedony), the Turkish chrysoprase reported by Ayvacıklı *et al.* (2012) and Hatipoğlu and Yardımcı (2014) should be included in this group rather than in the chrysoprase group. Similarly, the "new" bluish green variety from Africa (Renfro, 2015), which bears both Cr and V as likely chromophores, can be included in this group.

The third greenish blue variety is sold as "gem silica" or "chrysocolla chalcedony" and is coloured green by copper. Tiny inclusions of copper silicates have been indicated by Frazier and Frazier (1999) and by Laurs (2015). Also, Shen *et al.* (2006) clearly identified a Cu^{2+} band by UV-Vis-NIR spectroscopy.

Heliotrope (or bloodstone or plasma) is a dark green variety, dotted with small, hematite red, blood-like spots. The African variety is often called seftonite (Fig. 16) and frequently shows pyrite flecks. Heaney *et al.* (1994) attributed the green colour to the presence of tiny particles of chlorite or hornblende needles while Zhang and Sakurai (2009) vaguely connected the possible influence of Fe^{2+} and Cu compounds with the dark green colour, of Fe^{3+} (as hematite) with the yellow and red colours and of Fe_3O_4 with the black colour.

5.7. Pliny on green chalcedonies – description and provenance

The *chrysoprasus* mentioned by Pliny (*N.H.* 37, 77) is listed in the chapter dedicated to the varieties of *berullus*; therefore, it should be associated with a variety of emerald (chrysoberyl?) rather than chalcedony.

The gem "*iaspis*" is described as a green stone often translucent, thus being the only possible match with green chalcedony of some significance, although the term probably includes green jasper as well. According to Pliny the sources of *iaspis* were: (1) India, which provided a translucent variety resembling emerald; (2) Cyprus, with a hard and

Figure 16. Heliotrope (left, unknown photo credits) and "Seftonite" from South Africa (right, author's personal photo collection).

dull variety with greyish shades; (3) *Amisos* (modern Samsun on the south coast of the Black Sea, Turkey), where a variety similar to that from India was exploited; and (4) *Chalcedon* in Bithynia (modern Kadıköy, opposite Byzantium, south of Scutari), which supplied a "cloudy" variety (*NH* 37.115).

Regarding heliotrope, Pliny explains firstly the origin of its name (*N.H.* 37, 165): throwing the heliotrope in a container filled with water, the gemstone changed colour into blood-red when reflecting sunlight. Pliny adds that this property was particularly observed in the Ethiopian heliotrope and that the stone was often used to detect solar eclipses (this latter use was possibly correlated with the heliotropism). Lastly, Pliny ironically mocks the 'blatant effrontery' of the magicians who believed that the stone had the power to make someone invisible when used in conjunction with the homonym genus of flowering plants (*Heliotropium*, *Boraginaceae*). Regarding the distribution of heliotrope, Pliny listed Ethiopia, Africa and Cyprus as known supply areas (*NH* 37. 60.165).

The locations of European, African and Asiatic toponyms mentioned in this paragraph are shown in Fig. 17.

5.8. Modern supply areas

The main sources of chrysoprase are in Australia (Nagase *et al.*, 1997; Befi, 2009), often within weathered profiles resulting from lateritization of nickeliferous serpentinites or other ultrabasic rocks (Queensland; Krosch, 1990) but also in Kazakhstan (Sachanbinski *et al.*, 2001; Witkowski and Zabinski, 2004), Tanzania (Witkowski and Zabinski, 2004; Shigley *et al.*, 2009), Germany, Poland (Sachanbinski *et al.*, 2001; Skrzypek *et al.*, 2003, 2004; Čermáková *et al.*, 2017), Turkey (Hatipoğlu *et al.*, 2011b; Ayvacıklı *et al.*, 2012), Brazil (Komov *et al.*, 1994) and the United States (Arizona and California).

Recently, Serbia has been opening up gradually to the markets (Miladinović *et al.*, 2016). In Poland, chrysoprase was first identified in the 18th century from the Szklary mine; it was located within Ni-bearing serpentinites and has been exploited since the

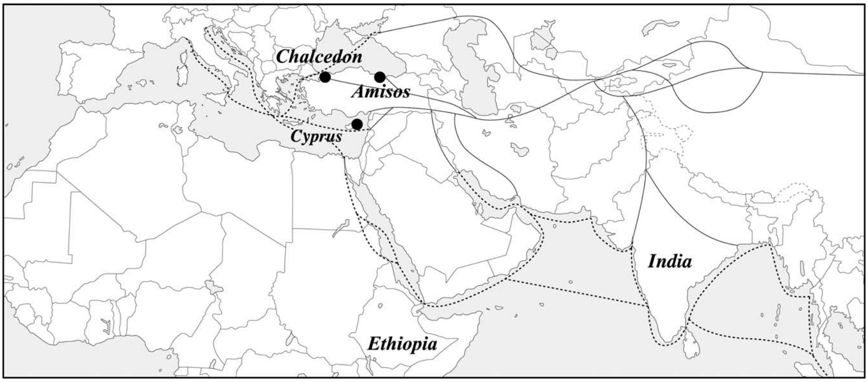

Figure 17. From the *Naturalis Historia* by Pliny the Elder: the distribution of chrysoprase, Cr-chalcedony and heliotrope. The silk road and the principal maritime routes are shown.

Middle Ages (Sachanbinski *et al.*, 2001; http://www.mindat.org/loc-232015.html). Further traces of ancient exploitation (Ottoman Empire Period) were found in the village of Dikmen, in the Biga–Canakkale region of Turkey (Hatipoğlu *et al.*, 2011b) and in the ancient Silesian territory (chiefly Frankenstein, Kosemütz Gläsendorf, Baumgarten with mines dated to the 14th century AD; Streeter, 2011).

In modern times, sources of Cr-bearing chalcedonies have been located at Saricakaya in Turkey (Eskisehir, Central Anatolia; Lule-Whipp, 2006), Tanzania (Hyršl, 2016), Zimbabwe (Smith, 1967), Bolivia (Hyršl and Petrov, 1998), the Balkans and the Ural mountains (Hyršl, 1999), as well as in the Newman area of Western Australia (formed by silicification of serpentinites; Willing and Stocklmayer, 2003), in Oregon (Riddle) and California, USA (Porterville, Exeter, Lindsay) (Frondel, 1962).

“Gem silica” or “chrysocolla chalcedony has been found in Arizona (Miami-Inspiration Mine; Globe District in Gila County, see Frondel, 1962), Peru, Namibia (Hyršl, 2016) and Spain (Laurs, 2015). Other mentioned sources are New Mexico, Mexico, Peru, Taiwan and the Philippines (https://geology.com/gemstones/gem-silica/).

Modern exploitation of heliotrope is concentrated in India (as carnelian and sard; *e.g.* the Kathiawar Peninsula mentioned by Frondel, 1962), China, Brazil, Uruguay, Madagascar, South Africa, Australia and the United States (Cavenago-Bignami Moneta, 1980). Frondel (1962) further enlisted Egypt among the areas of commercial exploitation and indicated Chatham Country in Georgia and Pony Butte in Jefferson County in Oregon as areas of occurrence.

5.9. The provenance of green chalcedonies in archaeometry and information gained from the geological literature

In the archaeometric literature, SR-XRD, Raman microspectroscopy and PIXE studies of three Cr-bearing chalcedonies and one heliotrope (from Vigna Barberini in Rome) are recorded (Gliozzo *et al.*, 2011). A single bead from Hepu county in China (one of the important ancient ports along the Maritime Silk Road) was characterized as a green chalcedony by Raman spectroscopy (Dong *et al.*, 2014) but no geochemical investigation was performed. Within the geological literature, two chrysoprases from the Biga–Çanakkale region in Turkey have been investigated by XRF and ICP-AES (Hatipoglu *et al.*, 2011b).

6. Chert, flint and jasper

“...a siliceous mineral, approaching in character flint, but less homogeneous and simple in character” (Lyell, 1830, on chert)

6.1. The distinction between chert and flint

The list of names, synonyms and definitions provided by Tarr (1938) is significant: chirt (Eng.), chert (Eng.), craie (Fre.), flint (Eng.), silex (Lat./Fre. = flint), silexite (Fre.), silex corne (Fre.) = horn flint (Eng.), silex de la craie (Fre.) = flint of the chalk (Eng.), Hornstein (Ger.), selce (Ita. = chert = flint), Phtanite (Gre. = chert), white chert (= chert), black chert (= flint), cherty limestone = siliceous limestone; *vlint* in Dutch; *flins* in old German, *flinta* in Swedish; vlint, vlynt, flent, flynd, and flyntee in old English; *pierre a feu*' (Fre.) = firestone (Eng.) = *Feuerstein (Ger.) = flint.*

It is surprising that Tarr (1938) observed that chert was a recent name if compared to flint and that, at the beginning, both terms were used synonymously to indicate the same material, in order to distinguish the darker (flint) from the lighter (chert) coloured varieties. With the passing of time, the term chert has been increasingly used to indicate an "impure" flint since Cayeux (1929) introduced the petrological association and occurrence of chert as a distinguishing factor, hence limiting the use of this term to siliceous rocks in marine deposits (*e.g.* radiolarian cherts). Due to American usage, flint was gradually abandoned in favour of chert and reserved for artefacts.

Nowadays, the use of these terms is still controversial depending on whether archaeological or geological literature is concerned. The term flint is commonly used in archaeological papers while it is very rare in geological ones. Regarding the definitions, there is a general consensus in relation to the fact that chert is the broad term, indicating large bodies of white or lightly coloured rocks, occurring in "soft" carbonates (*e.g.* limestone, dolostones), while flint is a variety of chert, occurring as nodules of dark microcrystalline quartz and originating in chalk and marl. On the other hand, it is accepted that flint and chert cannot be distinguished based on mineralogical characteristics, although Heaney and Post (1992) found that moganite contents ranged between 13 and 17% in flint (indicated as grey varieties characterized by a greasy texture) and between 5% and 75% in chert (indicated as all other non-fibrous varieties).

Both contain microcrystalline quartz, which may be associated with amorphous silica and opal, and a subordinate content of macrocrystalline quartz (Folk and Weaver, 1952; Folk, 1980; Heaney, 1993). Both contain up to 95% silica (Hesse, 1988) and, as has already been pointed out above, variable contents of moganite.

Based on Heaney and Post (1992), the granular texture of quartz should have been a discriminating factor between chert and chalcedony; this indication is often ignored, however, and chert is thus considered to be a mixture of both granular and fibrous quartz from microcrystalline to cryptocrystalline (excluding quartzite).

6.2. The distinction between chert and jasper

Chert can be of both organic (diatomite and radiolarite on ocean floors) and inorganic origins. Its formation can be due to different types of processes: (1) accumulation of siliceous oozes on the oceanic floors (diatomites and radiolarites); (2) secondary replacement of carbonate minerals (shallow marine deposits); or (3) precipitation from silica-rich hydrothermal solutions (silica sinters). A comprehensive review of the petrogenesis of chert was provided by Knauth (1994) while a clear nomenclature based on chert formation processes was adopted by Ledevin *et al.* (2014).

As stated above, chert can have grain size from macro- to cryptocrystalline and may include several types of silica polymorphs. Chert varieties include jasper, radiolarite and porcellanite.

Jasper is frequently defined as a variety of chalcedonic silica (*e.g. Oxford dictionary of Earth Science*); however, chalcedony is constituted by micro- to cryptocrystalline quartz and moganite only, while jasper may include both a mixture of micro- to cryptocrystalline quartz polymorphs and a significant amount of other materials (*e.g.* hematite, goethite, magnetite, chlorite, *etc*.; see Kostov, 2010); therefore, it is more appropriately classified as a variety of chert. Despite the numerous attempts made by many authors to outline the classification of jasper (see Kostov, 2010), there are still many unclear features regarding its composition (very heterogeneous) and origin (metamorphic or sedimentary; see Kostov, 2010). In recent publications, the use of the term jasper seems very limited and restricted to bedded chert, associated with banded iron formations.

Among chert varieties, the jasper/radiolarites can be further distinguished into black phtanite and lydite (or lyddites). Phtanite has been used from prehistory (see *e.g.* Tsobgou and Dabard, 2010 and Mosin and Nikolsky, 2010) as well as lyddite (also named Lydian stone), the latter being commonly identified with the touchstone.

6.3. Pliny on chert, flint and jasper

Pliny uses the term *silex* to indicate both marbles (*luniensem silicem*; *N.H.* 36, 135) and several varieties of tufa (*N.H.* 36, 168-169); similarly, the term *iaspis* includes both jasper and green-chalcedony, but also other pink (rose quartz?) and blue gems (blue quartz?, sodalite?). Similarly, it is difficult to propose a reliable match for several gemstones mentioned by Pliny such as the blood-red coloured *haematiti*, which may correspond to the red jasper.

As for touchstone, the composition of this stone is controversial because Pliny (*N.H.* 33, 135) refers to it as *basanites* and noted that some people call it ‘Lydian’ stone (‘Heraclian’ was omitted based on Cohen and Drabkin, 1958). Citing Theophrastos (*De Lap*. 47, 46), Pliny further specified that touchstone was initially found along the river *Tmolus*, but the *Tmolus* is not a river but a Lydian mountain (modern Bozdağ), famous for the electrum placers of the rivers *Pactolus* (see Midas Legend) and *Hermus*. The geology of the Bozdağ area is not characterized mainly by basalts; instead granitic augen gneisses, paragneisses and schists are common, together with minor migmatites (Hetzel *et al.*, 1998; van Hinsbergen, 2010).

Hence, the correlation between touchstone and basalt becomes weaker, although several Greek authors called it βάσανος (see *e.g.* Theognis 417). In this regard, the most interesting evidence has been provided by Moore and Oddy (1985), who determined petrographically that most touchstones were made of tuff, chert and siltstone.

On a final note, it is worth adding that: (1) the term lydite or ‘Lydian stone’ today indicates a variety of jasper/radiolarite; and (2) assuming that *haematitis* and red jasper are the same, Ethiopia, Arabia and Egypt should be listed among the supply areas.

6.4. Chert and flint provenance in archaeometry

The archaeometric literature is strongly orientated towards functional (*e.g.* Milot *et al.*, 2017), morphological (*e.g.* Rapp, 2002) and social features (*e.g.* Schmidt *et al.*, 2016) rather than compositional ones. This situation is probably a consequence of the limited results obtained so far in flint provenancing.

Archaeological and geological samples investigated scientifically amount to >792 samples of chert (~181 archaeological and ~611 geological) and 532 of flint (>220 archaeological and >309 geological) (Appendices 3 and 4), without counting those reviewed by Luedtke (1992).

In both France and the UK, chert/flint provenance has represented an attractive research topic for a long time but, apart from the systematic work performed by Bressy (2002) on French chert, most publications have presented the results of statistical treatments only. This is the case of Ferguson (1980) who applied data coding to the analytical results obtained by the geochemical examination of 15 British flint mines. Similarly, a geochemical study performed on black chert by means of ICP-AES, ICP-MS and LA-ICP-MS was performed by Evans *et al.* (2007) but raw data were not made available. The authors described black chert as a material "with similar qualities to flint but of inland limestone origin" and sampled archaeological artefacts from Mesolithic sites and two geological sources, respectively, in the northern (Fremmington Edge and Fell End Hush) and southern (Home Farm and Middleton by Youlgrave) Pennine limestones. Likewise, an interesting comparison between geological and archaeological flints was performed on 10 Israeli samples by means of instrumental neutron activation analysis (Frachtenberg and Yellin, 1992) but the raw data were not shown.

The same problem occurs with the geochemical investigations performed on: chert from various localities analysed by Brandl (2014, 2016) and Brandl *et al.* (2011, 2014); Montana chert (Roll *et al.*, 2005); "black chert" from northern England (Evans *et al.*, 2007, 2010); chert sources from the area of New York (Rafferty *et al.*, 2007); German cherts from the area of the Swabian Jura and Franconia Alb (Bressy and Floss, 2006); flint from several sites in the UK (Pettitt *et al.*, 2012) and many others.

The most substantial and conspicuous set of data concerns cherts from France (cited above) and North America, with more than 569 specimens investigated geochemically. Among this wide group, ~124 samples were of chert stone tools while the other 445 samples were representative of several chert sources. The former group includes cherts from the US states of Indiana (Glascock, 2004), Nebraska (Hoard *et al.*, 1993), Nevada (Morgenstein, 2006), North Dakota (Huckell *et al.*, 2011), Oregon (Hess, 1996; Morrow *et al.*, 1992) and Washington (Morgenstein, 2006).

The second group includes chert sources cropping out the US states of California (Murray *et al.*, 1991), Colorado (Hoard *et al.*, 1993; republished in Huckell *et al.*, 2011), Illinois (Hess, 1996; Morrow *et al.*, 1992), Indiana (Glascock, 2004), Kansas (Hoard *et al.*, 1993), Michigan (Luedtke, 1978), Nebraska (Hoard *et al.*, 1993; republished in Huckell *et al.*, 2011), Nevada (Morgenstein, 2006), North Dakota (Huckell *et al.*, 2011), Ohio (Luedtke, 1978; Glascock, 2004), Oregon (Hess, 1996), South Dakota (Hoard *et al.*, 1993; republished in Huckell *et al.*, 2011), Wahington (Morgenstein, 2006) and Wyoming (Hoard *et al.*, 1993; republished in Huckell *et al.*, 2011).

7. Quartz varieties

All quartz varieties are characterized by a macrocrystalline grain size (>1 μm). An exhaustive discussion on quartz would be too long for this review. In the field of quartz studies, the numerous and varied research studies are readily available; however, the studies by Frondel (1962), Heaney (1994) and Götze and Möckel (2012) are the key texts from which to start.

The following sections will focus on hyaline quartz, milky quartz, smoky quartz, amethyst, citrine, prasiolite, and rose, pink and blue quartz.

7.1. Hyaline quartz (rock crystal), milky quartz, smoky quartz (morion)

These three varieties are characterized equally by the presence of macrocrystalline quartz, the latter being the sole component of rock crystal. Rock crystal has been used for a long time as a gemstone, as is well testified by ancient literature (see below) as well as by more recent appellatives – often indicative of their provenances – such as the "Herkimer diamonds" (hereafter diamonds abbreviated as d.), "Lake George d." (New York) or "Marmaros d." (from the Maramaros County of the Kingdom of Hungary now corresponding to part of Romania and Ukraine), "Cape May d." and "Arkansas d." (New Jersey and Arkansa, USA), "Bristol d." and "Cornish d." (United Kingdom), "Briançon d." and "Alençon d." (France), "Schaumberg d." (Germany), *etc.* (Frondel, 1962).

The appearance of milky quartz is due to fluid inclusions entrapped in the crystal (Götze and Möckel, 2012), while the appearance of smoky quartz is due to aluminium (Al^{3+}) impurities substituting for silicon (Si^{4+}); the charge compensators being H^+, Li^+ or Na^+. The colour centre is indicated as $[Al_{Si}O_4/M^+]^0$, where Al is a substitute for Si, while M^+ stands for H^+, Li^+ or Na^+ (Martins Nunes and Soares Lameiras, 2005 with references therein). Only Li and Na can stabilize the colour centre, given that H^0 is not stable at room temperature (Götze and Möckel, 2012).

Further details and previous studies of smoky quartz were discussed by Frondel (1962) and Rossman (1994) while a comprehensive discussion of colour enhancement and dyeing of quartz was provided by Scholz *et al.* (2012).

7.2. Pliny on hyaline, milky and smoky quartz: description and provenance

Pliny provides a vast quantity of useful information about the use, formation and provenance of rock crystal but information about the other two varieties is very sparse.

Smoky quartz (*mormorion*: Pliny's misspelling for morion) is described briefly as a very dark translucent stone from India, also known as *promnion* or *Alexandrion* or *Cyprium*, depending on the presence of red shades (*N.H.* 37, 173).

Milky quartz may be identified with the *Galactitis*, which was an entirely milk-white stone produced along the Nile (Egypt) and the Achelous (western Greece) rivers (*N.H.* 37, 162).

Rock crystal (*crystallum* in latin) formed due to the intense cold, so that the places of discovery were limited to areas where snow freezes (Pliny, *N.H.* 37, 23). The Greek etymology of the word κρύσταλλος (meaning ice, frozen) was evidence advanced by Pliny in support of that theory.

Pliny (*N.H.* 37, 26) also questions why rock crystal forms hexagonal faces, admitting that both the lack of symmetrical terminations and the presence of completely flat faces complicate matters. Specimens without defects were called '*acenteta*' (lacking in core) by the Greeks and, in general, they were not carved.

The largest crystal that Pliny had ever seen weighed 150 pounds and was dedicated by *Livia* (wife of *Augustus*) in the Capitol; other authors referred to huge vessels made of this material, however (*N.H.* 37, 27). Besides these uses and others (*e.g.* jewellery and weapons), the practice of cauterizing wounds with rock crystal exposed to sunlight is also reported (*N.H.* 37, 28).

According to Pliny, competition from glass production had to be ruthless but uneffective; in fact, the value of rock crystal (mostly determined by its weight) increased.

Regarding the supply areas, Pliny (*N.H.* 37, 23-24) mentioned India, Asia Minor (Alabanda and Orthosia), Cyprus, the island called *Necron* (*i.e.* island of the Dead) in the Red Sea facing Arabia (maybe the island of Maceira), the neighbouring island of St. John (Egypt), Portugal (*Ammaeensibus iugis*, maybe close to the ancient town of Ammaia in the municipality of Marvão, along the border with Spain) and the European Alps.

Regarding Portuguese supplies, the geoarchaeological field campaigns performed around the imperial town of Ammaia established that rock crystal could have been extracted locally from at least three mine sites and especially in the Pitaranha granite quarry (Taelman *et al.*, 2009, 2010).

The Alpine deposits provided the best quality rock crystal but outcrops were found mostly in inaccessible places, so that the miners had to be suspended by ropes (Pliny (*N.H.* 37, 27). The ancient exploitation of the San Gottardo area is confirmed by modern geological investigations as well as by archaeological remains from both the Prehistoric and Roman ages (Donati, 1986a, 102). In this respect, the finding of two blocks of rock crystal in the Roman settlement of Locarno-Muralto is of particular interest (Donati, 1986b, 213–216). Traces of a likely Neolithic age exploitation have been further recognized in the upper Romanche Valley (Rostan, 2007), as well as in the southern department of Bouches-du-Rhône (Baroni, 2003) and in the northern and wider area of the Alpes du nord (Brisotto, 1999). Actually, the majority of archaeological findings and, as a consequence, of the archaeological studies were concentrated along the Alpine Arch from Switzerland to France (Della Casa, 2005). Other sporadic findings were included in the reports of several excavations (*e.g.* Andreozzi *et al.*, 1996).

As regards the type of outcrops, the news from *Xenocrates*, according to which rock crystal was pulled up by the plow in Asia Minor and Cyprus, left Pliny puzzled, while he was more inclined to accept the argument that it could be transported by streams (*N.H.* 37, 25). In the end, though, he returns to the initial assumption and concludes that rock crystal cannot be found in well irrigated areas but only in the presence of pure snow.

The locations of the toponyms mentioned by Pliny are shown in Fig. 18, except for Necron Island.

7.3. Past and current supply areas

As for past supply areas, traces of smoky quartz were found at Romit (Egypt) in a Roman gold mine (Aston *et al.*, 2000); however, the Alpine deposits must have been exploited since ancient times for both rock crystal and smoky quartz.

As for modern supply areas, rock crystal can be found in numerous sites all over the Mediterranean basin; major fields of extraction are located in Brazil (Minas Gerais), Russia (Ural Mountains), USA (Arkansas, Virginia, North Carolina and California) and, to a lesser extent, in Guatemala, Colombia, Peru, China, Nepal, Burma, Madagascar and Australia (see also Stoiber, 1945 and Frondel, 1962).

Beyond its wide distribution, the best smoky quartz gems are extracted in Brazil, USA (Colorado, New Hampshire and Arkansas), European Alps, Scotland, Madagascar and Mozambique; however, most of those currently available commercially have been irradiated. Occurrences have been reported in Piemonte, Switzerland, Scotland, Russia, Brazil, Madagascar, Elba island, Mozambique, and from Arkansas, California, Colorado, Maine, Montana, New England, New Hampshire, North Carolina, Texas and Utah in the USA (Frondel, 1962).

Milky quartz also occurs worldwide but its exploitation for commercial purposes is not only very limited but also scarcely known from the literature.

7.4. Hyaline, milky and smoky quartz provenance in archaeometry and the information gained from the geological literature

Archaeometry has scarcely approached the provenance issue of rock crystal. The studies conducted by Taelman *et al.* (2009, 2010) are of fundamental importance

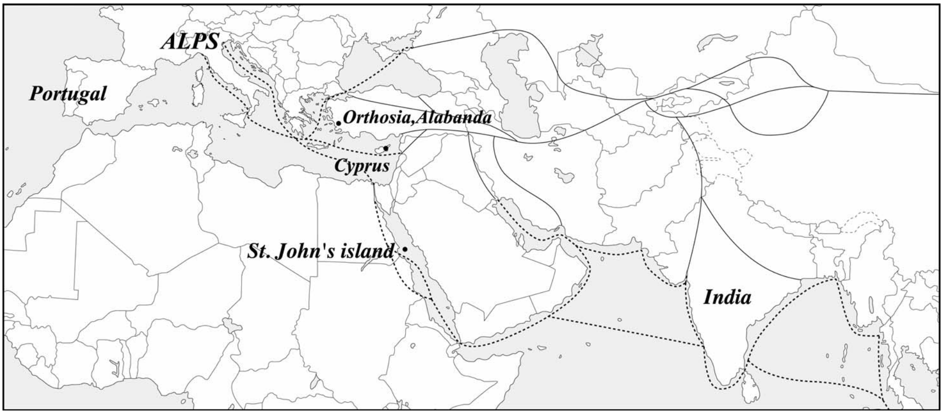

Figure 18. From the *Naturalis Historia* by Pliny the Elder: the distribution of hyaline and milky quartz. The silk road and the principal maritime routes are shown.

because they provide clear evidence of rock-crystal extraction sites, mentioned explicitly by ancient sources. Similarly, the studies conducted on lithic materials cropping out across the Alps are of great interest because they reconstruct the exploitation of this gemstone in a specific territory during a long time period such as Prehistory.

However, there has never been a specific focus on rock crystal and geochemical investigations are lacking; conversely, archaeometric studies focused mainly on fluid inclusions (see *e.g.* Cousseran *et al.*, 1998; Cousseran, 2000). Even the geological literature is of little help in this case.

7.5. Rose and pink quartz

There is a general tendency to distinguish the euhedral variety of pink quartz from massive rose quartz. The former is rare and clear while the latter is common and turbid.

The main distinguishing feature between these two varieties is represented by the sources of rose colour. As for pink quartz, the colour has been attributed to $\text{Al-O}^{-}\text{–P}$ hole centres induced by ionizing radiation (Maschmeyer and Lehmann, 1983a).

As for massive rose quartz, instead, several hypotheses have been disputed before arriving at a general consensus. The first hypothesis attributed the rose colouration to Mn^{3+} pigmentation (Holden, 1924a,b). The following hypothesis was based on the presence of rutile (Vultee and Lietz, 1956; Dennen and Puckett, 1971) and also Frondel (1962) assumed that rose quartz "typically" contained needle-like inclusions of rutile. Rutile, however, which is sometimes still mentioned in the literature, does not seem to be present in rose quartz. Between the 1960s and 1980s, research focused mainly on the presence of Ti^{3+} (Wright *et al.*, 1963; Cohen and Makar, 1984) and, especially, on the intervalence charge transfer between Ti or Fe and Ti as the main feature responsible for the rose colour (Smith *et al.*, 1978; Cohen and Makar, 1985).

Following studies by Ignatov *et al.* (1990), Smith *et al.* (1978), Alexander *et al.* (1986; on dumortierite), Hemingway *et al.* (1990) and Applin and Hicks (1987), Goreva *et al.* (2001) hypothesized that the $Fe^{2+}\text{–}Ti^{4+}$ intervalence charge transfer in dumortierite was responsible for the rose colour. Furthermore, they indicated iron reduction as being responsible for the colour changes from pink (Fe^{2+}) to colourless (Fe^{3+}) and to pink again (Fe^{2+}); the latter change being obtained by heating the colourless fibres under reducing conditions. However, the identification of dumortierite was not straightforward; the authors generally indicated this phase as the one that better matched the patterns obtained by means of various techniques (Goreva *et al.*, 2001). Only a detailed HRTEM study was able to provide an unambiguous characterization of these fibres, confirming their identification as dumortierite, characterized by a large amount of Fe substituting for Al in the M1 sites (Ma *et al.*, 2002).

Both rose and pink quartz are photochemically unstable (see also Rossman, 1994) and, thus, subject to fading. In pink quartz, fading was attributed to the $\text{Al-O}^{-}\text{–P}$ hole centres. The same explanation was given for rose quartz, although it cannot explain why soaking in water should return the rose colour to this quartz (Goreva *et al.*, 2001). The other possible explanation involved the expansion and shattering of CO_2 inclusions due to solar heat and the consequent scattering of light on a microfractured surface (Goreva *et al.*, 2001).

Further characterizing features are asterism and the tendency to darken when exposed to X-rays. Macroscopic inclusions of associated bismuthinite (Bi_2S_3) and chalcopyrite grains were reported in a rose quartz from Madagascar only (Hyršl and Danet, 2005).

Rose and pink quartz can be found in hydrothermal veins but they are mostly concentrated in granitic pegmatites, often associated with tourmaline, cassiterite, beryl and phosphate minerals (Cassedanne and Roditi, 1991; Goreva *et al.*, 2001). Major sources include Brazil, India, Madagascar and Sri Lanka, while Frondel (1962) further listed the occurrences reported in Canada (New England), California (Pala and Mesa Grande), Colorado (Scott quarry at Custer), Maine (Newry; Bumpus mine near Stoneham; Albany, Paris), South Dakota (Black Hills), South Africa (Rossing), Germany (Rabenstein) and Sweden (Långban; this containing durmortierite).

To the author's knowledge, there is no archaeometric research which has focused on these materials.

7.6. Pliny on rose and pink quartz

An exact match to the gems listed by Pliny is not traceable with certainty; therefore, it is only possible to make some assumptions.

It is reasonable to think that rose and pink quartz correspond to one of those gemstones that Pliny describes with various shades of colour. For instance, these varieties could be identified as a variety of amethyst, or a variety of sapphire, or the "mild carbuncle", *i.e.* a sub variety of the *carbunculus lychnis*, resembling the pink colour of the "Flower of Jove".

Rose and pink quartz could also be identified with one of the many Plinian gemstones that we cannot identify. This might be the case for the so-called *Aphrodisiaca* that had to be pink (Pliny, *N.H.* 37, 148: *Aphrodisiaca ex candido rufa est*). In fact, ancient and modern beliefs attribute the capacity to foster the search for a soul-mate for quartz. This property could be reflected in the name of the gem, which is referred to as "love stone" nowadays. Moreover, ancient mythology indicates rose/pink quartz as a tool in the hands of Cupid and Eros.

It is further known that rose quartz was used by the Assyrians to make beads and seals (Harper *et al.*, 1995) and by the Egyptians to make funerary vessels (Aston *et al.*, 2000) and talismans with the power to prevent aging (http://www.gia.edu/rose-quartz-history-lore). However, there are no evocative gemstone names related to these properties in the Plinian prose.

7.7. Amethyst, citrine and prasiolite

Amethyst is the purple variety of quartz and might be one of the most appreciated varieties in Antiquity. Recent X-ray absorption spectroscopy experimental data have established that Fe replaces Si in its tetrahedral site and occurs mainly in the trivalent state, although minor amounts of Fe^{4+}, responsible for the purple colour, may be present (Di Benedetto *et al.*, 2010 with references therein). Conversely, Czaja *et al.* (2017) have found Fe^{3+} only ("in interstitial positions in channels parallel or perpendicular to the *c* axis") in Polish amethyst and prasiolite. An earlier hypothesis and further details on amethyst's iron centres, synthesis, colour distribution and stability are included in Rossman (1994).

The yellow variety of quartz – citrine – is rare in nature and this is the reason why most citrine on the market is actually heat-treated (~500ºC) amethyst. Numerous authors agree in stating that the incorporation of trivalent iron (Fe^{3+}) and the colour centres are basically responsible for the yellow colour and are often associated with Al impurities (Samoilovich *et al.*, 1969; Lehmann, 1971; Nassau and Prescott, 1977; Maschmeyer *et al.*, 1980; Maschmeyer and Lehmann, 1983b; Balitsky and Balitskaya, 1986; Pan *et al.*, 2008). Other authors, instead, are inclined to believed that ~100 nm-sized iron particles play the major role in producing the yellow colour of natural citrine (Lehmann and Moore, 1966). Aines and Rossmann (1986) reported the selective dominance of molecular water or hydroxide ion in the citrine and amethyst sections of a dichromatic quartz, respectively. A comprehensive review of all these aspects was carried out by Rossman (1994) and, more recently, Nunes *et al.* (2013) stated that natural citrine is not affected or strongly affected by UV or gamma irradiation, respectively.

Prasiolite is the green variety of quartz. Today's prasiolite is generally obtained from heated amethyst (from Arizona, Brazil and Zambia; see Rossman, 1994 for more details); however, the same process is observed in nature (Paradise, 1982). In this regard, Herbert and Rossman (2008) established that naturally occurring green prasiolite is a radiation-induced colour variant of quartz (*i.e.* not just a heated pre-existing amethyst), which develops in the presence of specific chemical constituents and H_2O inclusions (from the nano- to the macro-scale).

Hence, irradiation of the system is a major factor in the development of amethyst, smoky and green colours in quartz while the presence of H_2O within the quartz structure has been found to be detrimental to the development of only certain colours (Aines and Rossman, 1986).

7.8. Pliny on amethyst

Pliny (*N.H.* 37, 121) narrates that the name amethyst was related strictly to its colour, being similar to that of wine; in fact, the Greek word αμέθυστος (= α μεθύω) literally means "not drunk". In Greek mytology, Amethyst was a nymph loved by Bacchus. She did not return his love and asked Diana to help her. The goddess of the woods transformed the nymph into a crystal and when Bacchus found her, he tipped his cup of wine over her in irritation, conferring the violet colour to that beautiful crystal. It is maybe not a coincidence that modern crystal therapy uses amethyst to fight against obsessive craving for alcohol, tobacco and drugs, as well as to control the temperament and to reduce work stress and insomnia.

Pliny further adds that this gemstone was violet and transparent but not so dazzlingly brilliant as *carbunculus* and was difficult to engrave (*N.H.* 37, 121).

A variety was named *socondios* by the Indians as it had the characteristic colour of the hyacinth (*N.H.* 37, 122 and 125). This variety may correspond to the actual wisteria amethyst, considering that wisteria/glicine had not yet arrived in Europe at the time of Pliny. A fainter variety was the *sapenos* or *pharanitis*, the latter taking its name from a tribe on the border of Arabia where it was produced. This reference is likely to be linked with the town of Pharan, which was 6 miles distant from Mount Choreb, at the foot of Mount Serbal, in the Sinai Peninsula (Cosmas Indicopleustes, *Christian Topography*, Book V). A further variety is represented by a bi-coloured amethyst which turns from violet to colourless, thus resembling rock crystal (*N.H.* 37, 123).

Pliny further mentions (*N.H.* 37, 123) at least three synonyms for amethyst which were *paederos* (*i.e.* lovely youth or favourite; already used for opal at *N.H.* 37, 84), *anteros* (*i.e*. avenger of slighted love or love unrequited) and *Veneris gena* (*i.e*. Venus eyelid).

Similarly to the heavy criticism expressed during the description of agate, Pliny railed against the widespread belief of magicians whereby amethyst would prevent drunkenness, ensure access to the presence of kings, avert hail as well as the attacks of locusts (if combined with a special prayer) and protect from spells; in the latter case, however, the gemstone would have been inscribed with the names of the sun and the moon, suspended from the neck, and worn together with some hair of the cynocephalus (a kind of baboon) and swallow feathers (*N.H.* 37, 124).

As for provenance, Pliny stated that it mainly came from India but also from the region of Arabia known as Petra (maybe Jordan), Lesser Armenia, Egypt, Galatia, Thasos and Cyprus; the last two areas providing the worst quality and the least valued amethyst (*N.H.* 37, 121).

The locations of the toponyms mentioned by Pliny are shown in Fig. 19, except for the town of Pharan.

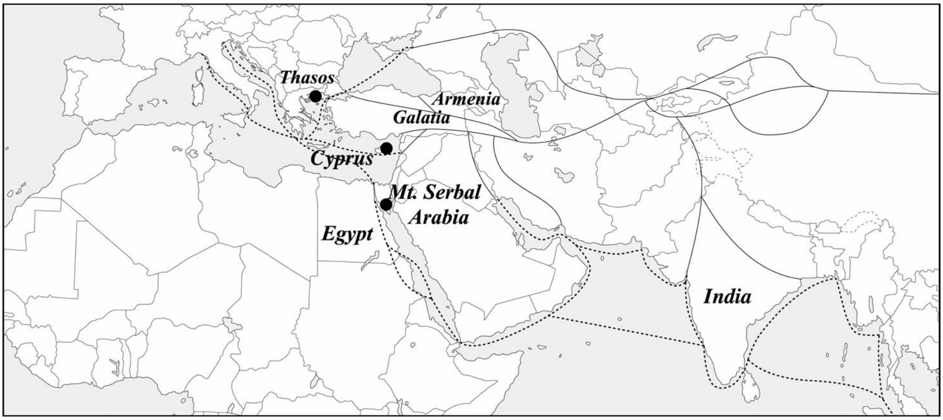

Figure 19. From the *Naturalis Historia* by Pliny the Elder: the distribution of amethyst. The silk road and the principal maritime routes are shown.

7.9. Past and current supply areas

Amethyst is a very common gemstone which occurs in deposits of varied nature throughout the world. It can be found in hydrothermal veins (*e.g.* Guanajuato in Mexico and Porkura and Macskamezö in Romania; reported by Frondel, 1962), in Alpine type veins, in cavities of pegmatites and granites, in hematite deposits and, especially, in basic igneous flow rocks such as basalts (Frondel, 1962).

Russian (Ural mountains, *e.g.* Olkhovka and the Reshev and Alapayev districts around Mursinsk mentioned by Frondel, 1962) and German (Idar-Oberstein) amethyst, now largely exhausted, has given way to Brazilian amethyst (especially from Rio Grande do Sul and Bahia; see Scholz *et al.*, 2012 for further details), at least since 1727 (date reported by Frondel, 1962). Past exploitation has also been recorded in Bohemia (Krušné hory mountains; see Řehoř, 2009), France (Puy-de-Dôme), Nova Scotia and Ontario (Thunder Bay) in Canada, and many other localities in the UK, Georgia, Arizona, Colorado, North Carolina, Pennsylvania, Virginia and Wyoming (Frondel, 1962) while current deposits are also located in Zambia, Mexico, and Uruguay. Smaller deposits are located in Australia, Sri Lanka, India, Madagascar, southwest Africa and the United States (Webster, 1983; Epstein, 1988).

Similarly, most citrine and prasiolite – both very rare – are derived mainly from Brazil (Bahia, Minas Gerais) but other occurrences have been registered in Colombia (San Cristobal, Santander), Spain (Salamanca) and France (Dauphine). As for the zones where natural citrine mainly occurs, Rossmann (1994) also listed Hyderabad in India and the Anahí mine in Bolivia while Frondel (1962) also mentioned Madagascar, the Isle of Arran in Scotland, the province of Salamanca in Spain, the Dauphiné in France, the territory of Mursinsk in Russia and North Carolina in the United States.

Prasiolite has also been found in Poland (Suszyna–Mrówieniec area and Płóczki Górne; Platonov and Szuszkiewicz, 2015 with references therein), Canada (Thunder Bay), Namibia (Farm Kos and Farm Rooisand) and Zambia (Kalomo-Mapatiqya), respectively; see Herbert and Rossman, 2008).

7.10. Amethyst, citrine and prasiolite provenance in archaeometry and the information gained from the geological literature

Geochemical studies of these gemstones are very rare to the author's knowledge; an accurate study was performed on a single sample of amethyst from Lauterbach in Germany (Götze *et al.*, 2001, reporting neutron activation analysis data from Haake and Holzhey, 1989).

7.11. Blue quartz

Blue quartz is relatively rare, generally translucent and with a waxy or greasy lustre. The origin of the blue colour remains a subject of active debate. Rayleigh scattering by submicron-sized inclusions (Jayaraman, 1939) is generally regarded as being responsible for the blue colour (see also Frondel, 1962 and Rossman, 1994 for further details). The inclusions can be of a very different nature but, among the numerous possibilities, rutile seems to be by far the most common type (Seifert *et al.*, 2011 with references therein). Among other possible inclusions, aerinite, apatite, biotite, ilmenite, muscovite, rutile, tourmaline and zircon have been mentioned (Iddings, 1904; Frondel, 1962; Parker, 1962; Barker and Burmester, 1970; Zolensky *et al.*, 1988; Romero Silva, 1996; Bartovics and Beane, 2007).

Seifert *et al.* (2009, 2010, 2011) provided extensive results on blue quartz inclusions (types, sizes, and frequencies, origin and thermal history). Those authors found abundant submicron-sized (1 μm–100 nm) inclusions of (probably syngenetic) mica, ilmenite and rutile and nanometre-sized (<100 nm) inclusions of (probably epigenetic) rutile; which of these might be responsible for the blue colour was not established, however.

The occurrence of blue quartz is limited to igneous rocks, mostly felsic, and their mildly-to-moderately metamorphosed equivalents (Seifert *et al.*, 2011). There are only a few areas where it has been recognized such as Spain (Romero Silva, 1996), Scandinavia, Norway (Goldschmidt, 1954), Virginia, USA (Wise, 1981) and India (Jayaraman, 1939). Frondel (1962) further stated that blue quartz was widespread in both igneous and metamorphic rocks from India (especially in the charnockite series, Champion gneisses of Mysore), Massachusetts, Pennsylvania (Baltimore gneiss), Rhode Island (Milford granite), Virginia (Ti-bearing rocks in the Amherst and Nelson counties; quartz diorite in Stafford county), New England (all USA), Sweden (granites), Finland (rapakivi) and Australia (albitite).

7.12. Pliny on blue quartz

Blue quartz may have been included in the description of other gems with the same colour. For instance, it may correspond to blue *sardonyx* (*N.H.* 37, 87 and 89) as well as to certain varieties of blue *iaspis* (*caeruleus iaspis*; NH 37, 115-116).

The problem is complicated further by the identification of lapis lazuli and azurite. It is well known, in fact, that lapis lazuli was called *sappirus* while azurite was called *lapis Armenius*; many modern authors share the view, however, that lapis lazuli was also called *Cyanus*, based on a well known Plinian text (*N.H.* 37, 119):

> "*We shall now give a separate account of cyanus, for a short time ago we applied the name to a iaspis owing to its blue colour. The best kind is the Scythian, then comes the Cyprian and lastly there is the Egyptian. It is very commonly counterfeited by tinting other stones, and this is a famous achievement of the kings of Egypt, whose records also mention the name of the king who first tinted stones in this way. Cyanus too is divided into male and female varieties. Sometimes inside cyanus there is a golden dust, which, however, differs from that which occurs inside the sappirus; for there the gold glistens as dots*" (Eichholz, 1962).

Indeed, this passage is controversial because it seems that Pliny – here summarizing Theophrastos (*De Lap.* 55 on ultramarine) – confuses the Egyptian production of the blue azurite pigment with both lapis lazuli and maybe the other varieties (the 'female' for instance) for which he fails to provide additional descriptions. However, it seems that Pliny does not want *cyanus* and *sappirus* to be considered as the same gemstone, although both may show golden inclusions.

The supply areas mentioned by Pliny are Scythia (*i.e.* the ancient region including part of Afghanistan, Bulgaria, Iran, Kazakhstan, Pakistan, Poland, Romania, Russia, Tajikistan, Ukraine, Uzbekistan), Cyprus and Egypt; however, the latter can be ruled out on the basis of the clear reference to azurite. Actually, Persia was the supply area of lapis lazuli, Scythia of cianos and sucina, and Cyprus of *adamas*, amethyst, *cyanus*, rock crystal, *iaspis* and *paederos*.

Also this indication of the supply areas does not find an exact match and then leaves open the suspicion that *cyanus*, like *caeruleum iaspis*, can actually correspond to blue quartz (but also to sodalite).

7.13. Current supply areas, archaeometric studies and geological literature.

Today's extraction sites are located in Brazil, Austria, South Africa and the USA (Virginia). Small occurrences have been documented close to Bologna (Val del Sillaro) in Italy but also in Spain, Sweden, Switzerland and the United Kingdom, and in numerous other countries (http://www.mindat.org/min-26723.html).

As for archaeometry, an exemplar of a blue quartz engraved gemstone (heron and palm) was found at Sevilla, during the archaeological excavation of a burial site dated to the end of the first century CE (years 80–90). The ring was investigated by Enrique Magario *et al.* (2002) using several techniques (optical microscopy, SEM-EDX, XRD, XRF and PIXE).

8. Final remarks

First of all, it seems clear that there should be a greater focus on the use of terms and in the determination of moganite. Ignoring this phase has clearly led to confused results concerning the identification, origin and occurrence of these materials. Also the definition of chromophores (elemental state/mineralogical phases) and of colour centres is not conclusive, especially as regards the quartz varieties.

As for archaeometry, the characterization and provenance issues have reached different stages of development.

Characterization is typically performed by means of a plethora of analytical techniques which are able to ensure accurate results, mostly in a non-destructive operational mode. However, the striking advances made in thermoluminescence and optically stimulated luminescence dating and use-wear of flint are counterbalanced by a far more simplistic approach in terms of the material characterization. In fact, it is common practice to limit research to phase identification – generally *via* Raman spectroscopy or portable X-ray fluorescence – neither of which is able to characterize the materials in an adequate and complete manner. Only in combination with geochemical analysis can sufficient information about the constituent elements be obtained – which may prove to be discriminant for provenance issues – and the possible treatments undergone by the gemstones established (*e.g.* use of metal tools used for surface treatments).

As for provenance, the scarce amount of geochemical data available from silica-based gemstones and chert does not allow the scientific community to achieve significant results in this field. Moreover, the reluctance to publish raw data and the large number of analytical techniques used by authors has complicated matters. As a result, a certain scepticism has spread among the community about the possibility and/or utility of performing such studies.

The handful of references quoted in the various paragraphs above should lead us to avoid reaching pessimistic conclusions and to encourage exploration in this lesser-known field of study.

A common analytical procedure should be followed in order to produce comparable results. In this instance, the main criteria should be the accuracy of the results, the non-destructive or minimally-destructive character of the analytical techniques and the instruments availability. The selection may be thus narrowed to the following techniques:

- Raman microspectroscopy and XRD for phase identification and quartz:moganite ratio quantification;
- Field emission scanning electron microscopy (FESEM), Environmental scanning electron microscopy (ESEM), or Scanning electron microscopy (SEM) for the determination of the amount of SiO_2;
- Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), for the determination of minor and trace elements; the *REE*s being especially important as they are mostly immobile and their patterns provide evidence of their environment of deposition.

Undoubtedly, there are some interchangeable techniques; *e.g.* SEM could be replaced by electron probe microanalysis (EPMA), which is destructive, however, or better, Particle Induced X-ray Emission (PIXE), or a non-destructive technique, able to provide accurate results, reaching a greater penetration depth than SEM-based techniques but definitely less widespread.

The determination of the quartz:moganite ratio may prove to be an important tool for the creation of a systematic classification of both chalcedony and chert but it may also provide important discriminant features to be used for provenance issues.

A further key point is represented by the need to create reference data and a database. The operation is complex and laborious and therefore opposed by many but it is undeniable that, in terms of provenance issues, archaeometry is able to provide answers only by comparison. Moreover, given the widespread distribution of these materials (as with many other objects of archaeometric interest), it is unthinkable that each individual researcher or research group should analyse each archaeological object so as to be able to compare data obtained personally only. Such an attitude is detrimental to the progress of a discipline (not only gemstones and chert) where there is a much greater need for accurate data than for review.

A further aid arrives from geological studies, which can provide useful data on natural outcrops to be used for comparison. Moreover, a better understanding of several issues involving precipitation, nucleation, diagenetic transformation and alteration of silica-based varieties, together with a more extensive and in-depth knowledge of the outcrops could provide important clues on raw material exploitation and marketing.

Meanwhile, Pliny has left us much information which should be autoptically verified, with targeted 'gem-hunting' campaigns. Pliny had no intimate knowledge of minerals and this is the reason why he followed the observations made by his colleagues and used the same name for different minerals. A revision of ancient gemstone names mentioned by both Latin and Greek authors will surely provide further insight into this topic; however, we cannot expect total clarity by ancient authors when such clarity is not even present in scientific texts today.

The Indian provenance of most precious gemstones cited by Pliny deserves a final comment. This should be considered as nothing more than a stereotype invented by merchants and, as such, should not be given much credibility. Based on the popular belief according to which the stones 'grew' better in warm climates, merchants tended to indicate India as the place of origin of the most beautiful stones. Hence, we have a well designed merchandising business which, on the one hand, exploited what today would be the name of a famous brand (*i.e.* the good name of India) and, on the other hand, helped to increase public awareness of the brand itself and, especially, line the pockets of merchants. Moreover, it is worth observing that most supply areas were: (1) repeated frequently by Pliny; and (2) situated along the principal commercial trade routes. Indeed, it is surprising that inland areas are almost never mentioned by Pliny when in fact the results of the archaeometric investigations clearly attest to their exploitation. This scenario seems to indicate that, in addition to popular belief, the origins of the gems were mostly related to the trade routes involved in their commercialization as well as to the nationality of the traders.

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Abbreviations and references

Nat.Hist. (*N.H.*) = *Naturalis Historia* (Pliny the Elder)

Lapid. = *De Lapidibus* (Damigeron).

ORPH.L. = *Orpheos Lithika Kerigmata* (in Greek). 1881. – In: Orphei Lithica. Accedit Damigeron De Lapidibus (Rec. E. Abel). 1881. Berolini, Calvary.

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Appendix 1. Geochemical analyses available for 287 samples of opals (25 archaeological; 262 geological). In the first column: A indicates archaeological objects; G indicates geological literature. The analytical technique used for opal characterization is specified in the last column.

	No. of samples investigated	Country	Reference	Analytical technique
A	25	USA	Hess (1996); Cummings *et al.* (1989)	NAA
G	150	Australia	McOrist *et al.* (1994); McOrist and Snallwood (1997); Gaillou *et al.* (2008a,b)	NAA
G	6	Brazil	Gaillou *et al.* (2008a,b)	ICP-MS
G	1	Canada	Amelin and Back (2006)	ICP-MS
G	8	Ethiopia	Gaillou *et al.* (2008a)	ICP-MS
G	7	Honduras	Gaillou *et al.* (2008a,b)	ICP-MS
G	5	Italy	Caucia *et al.* (2012)	ICP-MS
G	3	Kazakhstan	Gaillou *et al.* (2008a,b)	ICP-MS
G	4	Madagascar	Simoni *et al.* (2010)	LA-ICP-MS
G	11	Mexico	Gaillou *et al.* (2008a,b)	ICP-MS
G	2	Peru	Gaillou *et al.* (2008a,b)	ICP-MS
G	11	Slovakia	Gaillou *et al.* (2008a,b); Caucia *et al.* (2013)	ICP-MS; LA-ICP-MS
G	2	Tanzania	Gaillou *et al.* (2008a,b)	ICP-MS
G	2	Turkey	Karacik *et al.* (2011)	ICP-MS
G	50	USA	Cummings *et al.* (1989); Murray *et al.* (1992); Amelin and Back (2006); Gaillou *et al.* (2008a,b)	INAA; XRF; ICP-MS

Appendix 2. Geochemical analyses available on ~354 samples (183 archaeological and 171 geological) of agates and chalcedony varieties (mostly carnelians). In the first column: A indicates archaeological objects; G indicates geological literature. The analytical technique used for opal characterization is specified in the last column.

	No. of samples investigated	Country	Reference	Analytical technique
A	15	Afghanistan	Law *et al.* (2012)	NAA
A	52	Cambodia	Carter and Dussubieux (2016)	LA-ICP-MS
A	30	India	Law *et al.* (2012)	NAA
A	15	Iran	Law *et al.* (2012)	NAA
A	11	Italy	Gliozzo *et al.* (2011)	PIXE
A	16	Lybia	Gliozzo *et al.* (2014)	LA-ICP-MS
A	3	South Africa	Wadley *et al.* (2017); Prinsloo *et al.* (2017)	XRF
A	41	Thailand	Law *et al.* (2012); Carter and Dussubieux (2016)	NAA; LA-ICP-MS
G	1	Brazil	Götze *et al.* (2001)	NAA
G	4	Canada	Götze *et al.* (2001)	NAA
G	8	Czech Republic	Götze *et al.* (2001)	NAA
G	34	Germany	Götze *et al.* (2001, 2009, 2015, 2016)	NAA; ICP-MS; LA-ICP-MS
G	30	India	Carter and Dussubieux (2016)	LA-ICP-MS
G	17	Iran	Carter and Dussubieux (2016)	LA-ICP-MS
G	2	Lesotho	Prinsloo *et al.* (2017)	XRF
G	2	Mexico	Götze *et al.* (2001, 2015)	NAA; ICP-MS; LA-ICP-MS
G	1	Namibia	Götze *et al.* (2001)	NAA; LA-ICP-MS
G	6	Poland	Möckel *et al.* (2009); Götze *et al.* (2015)	LA-ICP-MS
G	17	Thailand	Carter and Dussubieux (2016)	LA-ICP-MS
G	27 or more	Turkey	Parali *et al.* (2011); Hatipoglu *et al.* (2011a); Koralay and Kadıoğlu (2015)	XRF; ICP-AES; XRF/ ICP-MS?
G	2	UK	Götze *et al.* (2001)	NAA
G	20	USA	Götze *et al.* (2009, 2015)	LA-ICP-MS

Appendix 3. Geochemical analyses available for ~814 samples of chert (181 archaeological; 633 geological). In the first column: A indicates archaeological objects; G indicates geological literature. The analytical technique used for opal characterization is specified in the last column. Unclear quantification in Hoard *et al.* (1993).

	No. of samples investigated	Country	Reference	Analytical technique
A	11	Belize	Cackler *et al.* (1999)	INAA
A	33	France	Speer (2014)	LA-ICP-MS
A	13	Lybia	Gliozzo *et al.* (2014)	LA-ICP-MS
A	~124	USA	Julig *et al.* (1991; Morrow *et al.* (1992; Hoard *et al.* (1993); Hess (1996); Glascock (2004); Morgenstein (2006); Huckell *et al.* (2011)	INAA; ICP, ICP-MS
G	3	Canada	Baldwin *et al.* (2011)	LA-ICP-MS
G	17	China	Chang *et al.* (2009)	XRF; ICP-MS
G	17	China	Peng *et al.* (2000)	NAA
G	25	China	Wang *et al.* (2012)	XRF; ICP-MS
G	8	China	Fang *et al.* (2017)	ICP
G	42	Croatia	Halamić *et al.* (2001)	XRF, ICP-MS
G	5	France	Becq-Giraudon *et al.* (1992)	XRF; ICP
G	14	Italy	Manetti *et al.* (1979); Di Leo *et al.* (2002)	INAA; XRF
G	9	Poland	Migaszewski *et al.* (2006)	ICP-AES; FAAS
G	2	Slovakia	Misik (1996)	Spectral analysis
G	1	South Africa	Prinsloo *et al.* (2017)	XRF
G	23	Turkey	Eker *et al.* (2012)	ICP-MS
G	22	UK	Armstrong *et al.* (1999)	ICP-MS
G	~445	USA	Luedtke (1978); Julig *et al.* (1991); Morrow *et al.* (1992); Hoard *et al.* (1993); Hess (1996); Glascock (2004); Morgenstein (2006); Huckell *et al.* (2011)	INAA; ICP, ICP-MS

The numerous cherts analysed by Bressy (2002) are not listed.

Appendix 4. Geochemical analyses available for >532 samples of flint (>220 archaeological; >309 geological). In the first column: A indicates archaeological objects; G indicates geological literature. The analytical technique used for opal characterization is specified in the last column. Data review in Luedtke (1992) not included.

	No. of samples investigated	Country	Reference	Analytical technique
A	35	Belgium	Moreau *et al.* (2016)	LA-ICP-MS
A	~32	France	Gratuze *et al.* (2001); Bressy (2002)	LA-ICP-MS; ICP-MS
A	4	Germany	Moreau *et al.* (2016)	LA-ICP-MS
A	45	Israel	Nathan *et al.*, 1999; Ekshtain *et al.* (2017)	ICP-MS, ICP-OES; ACP-AES, ICP-MS
A	8	Italy	Moroni and Petrelli (2005)	LA-ICP-MS
A	18	Russia	Olofsson and Rodushkin (2011)	ICP−SFMS, MC−ICP−MS
A	17	Spain	Prudêncio *et al.* (2016)	INAA
A	35	The Netherlands	De Bruin *et al.* (1972)	INAA
A	>26	UK	Aspinall and Feather (1972)	INAA
A	3	Ukraine/Moldavia	Kasztovszky *et al.* (2008)	PGAA
G	7 (sources)	Denmark and Sweden	Hughes *et al.* (2012)	EDXRF
G	~104	France	Bressy (2002)	ICP-MS
G	183	Israel	Nathan *et al.*, 1999; Ekshtain *et al.* (2017)	ICP-MS, ICP-OES; ACP-AES, ICP-MS
G	2	Italy	Schmidt *et al.* (2012a)	LA-ICP-MS
G	6	Poland	Kasztovszky *et al.* (2008)	PGAA
G	7	Spain	Prinsloo *et al.* (2017); Prudêncio *et al.* (2016)	XRF; INAA