

XRPD patterns of opals: A brief review and new results from recent studies

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A new classification of opals through X-ray powder diffraction (XRPD) methodology, by analysing 75 new samples of opal came from different worldwide areas, is introduced. A brief historical summary of the application of XRPD analysis on opals and the most important XRPD results reported in literature were compared with the newly obtained XRPD data. A simple method for the classification of opals on the basis of their degrees of structural order-disorder calculated from the diffraction data is proposed. In addition, a clear boundary, which has not been previously described by others in literature, related to the presence (or absence) of two-peak characteristic of the cristobalite phase is identified. This boundary allows for a discrimination of opals C from CT. © 2010 International Centre for Diffraction Data. [DOI: 10.1154/1.3478554]

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I. INTRODUCTION

Until the 1930s opals were considered, based on their physical and optical properties, as typical examples of amorphous matter, similarly with glass and other hydrogel colloidal materials (Garavelli, 1964). This assumption was also supported by the first X-ray powder diffraction (XRPD) investigations on samples of hydrophane, hyalite, and milk opals that showed the presence of just two diffraction peaks, i.e., typical of synthetic glass or liquid materials (Rinne, 1924). Similarly, other authors carried out XRPD investigations on opals and did not identify any lines on the films or, at best, identified only some weak interferences (Kerr, 1924). Even Baier (1932), into his long article about the optical properties of opals, underlined that it was not possible to observe any crystalline phases through XRPD analyses of opals.

However, following investigations showed that some diffraction peaks could be observed in several types of opals, which were more intense than the weak broad diffraction peaks typical of glasses. In an XRPD study of opals, silica glass, and silica gel, Levin and Ott (1933) reported for the first time that these anomalies were attributed to the presence of cristobalite. This high-temperature phase of silica was effectively identified, together with small amounts of quartz, in different samples of common opal, fire opal, and wood opal. Levin and Ott (1932, 1933) also highlighted the existence of completely amorphous opals such as hyalite and geyserites that showed in their XRPD patterns a broad peak at ~ 4 Å, typical of silica glass or artificial silica gel. Levin and Ott (1933) and Dwyer and Mellor (1934) were the first to make a classification of the opals on the basis of their crystallinity. For this reason these authors have always been considered as pioneers in the investigation of opals through X-ray diffractometry (Taliaferro, 1935; Cirilli and Giannone, 1941; Fenoglio and Sanero, 1943; Raman and Jayaraman, 1953;

Flörke, 1955; Frondel, 1962; Garavelli, 1964; Jones and Segnit, 1971; Mitchell and Tufts, 1973; Wilson *et al.* 1974; Graetsch, 1994; Smith, 1998).

With the development of more sophisticated technologies, several other authors continued their investigations of opals, substantially confirming the results of previous studies but also producing new results and theories (Wilm *et al.* 1934; Taliaferro, 1935; Laves, 1939). For instance, some authors have reported the occurrence of the β phase of cristobalite in opals (Greig, 1932; Sosman, 1932; Dwyer and Mellor 1932, 1934). Consequently, it was suggested that opals enclosed crystallites of high-temperature cristobalite.

Due to the increasing interest of the scientific community about the opal crystallinity, several investigations were carried out on this topic. The presence of α - and β -cristobalite was therefore hypothesised in several samples of opals from different areas (Cirilli and Giannone, 1941). However, the interpretation of the origin of cristobalite in opals was very controversial, especially because the mechanism of evolution of the silica gel into a crystalline state, at natural conditions, was still unknown.

Fenoglio and Sanero (1943) carried out X-ray investigations on their rich collection of opals from magnesite ores in the Piedmont Alpine foothills and observed that the enclosed β -cristobalite was characterised by a relatively low degree of crystallinity.

Further researches highlighted that two different phases of silica, characterised by d basal spacings of 4.04 and 4.11 Å, occurred in several types of opals. These two different phases implied a high and a low degrees of order and were interpreted as α - and β -cristobalite, respectively, because the former showed a lower symmetry with respect to the latter, which has cubic symmetry (Raman and Jayaraman, 1953). However, it was still unexplained how, in the same microcrystalline sample of opal, both the high- and low-temperature phases of cristobalite might be present.

The publication of the work by Flörke, “*Zur frage des hoch-cristobalit in opalen, bentoniten und gläsern,*” in the 1955s was particularly significant for the modern interpretation of the XRPD results on opals. The analyses reported in this work were carried out using a high-resolution instru-

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ment, which allow for the identification of diffraction peaks of tridymite. It was therefore assessed that, in natural opals, tridymite could be present together with low-temperature cristobalite (α -cristobalite). Tridymite and cristobalite in opals do not occur as individual crystallites: areas with stackings corresponding to cristobalite occur together with others corresponding to tridymite. This structure is typical of a strong disorder (Flörke, 1955).

The reasons preventing a recognition of the presence of α -cristobalite, exchanging it often for β or that led to the assumption that both α -cristobalite and β -cristobalite could be present in the same sample of opal, were probably because of the fact that many of the diffraction peaks of tridymite overlap with those of α -cristobalite.

As confirmed by many his contemporaries (Wahl *et al.*, 1961; Frondel, 1962; Jones *et al.*, 1963, 1964; Jones and Segnit, 1971; Wilson *et al.*, 1974; Mizutani, 1977) and by modern authors, the contribution of Flörke for an understanding of the complex α -cristobalite/ α -tridymite mixture, connected to the structural order/disorder in opals, was of fundamental importance. Performing photometric curves on the Guinier data, Flörke also observed a strong diffraction peak at $d=4.3$ Å, which he correctly attributed it to the (200) reflection of tridymite. We have to point out that this interference had been previously observed also by other authors (Levin and Ott, 1933; Wilm *et al.*, 1934), although they did not interpret it correctly probably because it was related, through a dense darkening, to the (111) peak of cristobalite. In particular, the interference observed in the Debye-Scherrer data was wrongly interpreted as a split of the (111) interference due either to the modalities of sample preparation or to an overlap of the diffuse band of the amorphous component.

In conclusion, Flörke observed that, with an increase in disorder, the X-ray patterns becoming more poorly defined, there was the emergence of a strong band characteristic of α -tridymite, while several interferences typical of cristobalite tended to disappear. Flörke (1955) also explained the shift of the main peak of cristobalite towards that of tridymite because of an increase in disorder.

The important work of Garavelli (1964) *Ordine e disordine negli opali* ("Order and disorder in opals"), concerning a large number of analyses on several types of opals, represented the "Italian" answer to the studies of Flörke, which were considered as milestones in this field of research. Garavelli confirmed the subdivision of opals in two types based on their degrees of structural order. In particular, he included into the disordered type the opaline silica of biogenic origin, the noble opals, the limpid hyalites, and the geysersites. In the ordered type Garavelli included the common opals, the xiloid opals, and the various types of "resinite" opals. He also observed that a small number of opals showed intermediate characteristics between the ordered and the disordered groups.

A true classification of opals was elaborated only in 1971 when Jones and Segnit in their work *The nature of opal-nomenclature and constituent phases* presented a classification of opals that today, almost 40 years after, is still being used. Until then, the preceding classifications substantially divided opals in two groups, ordered and disordered (as described above); even the existence of intermediate characteristics was recognised (Levin and Ott, 1933; Dwyer and

Mellor, 1934; Flörke, 1955; Garavelli, 1964).

Conversely, based on the results of their previous works (Jones *et al.*, 1963, 1964) Jones and Segnit identified three well-defined typologies or structural groups of opals. Even if this classification appeared to be very simple, it turned out to be correct and was accepted by the scientific community. As a matter of fact, this classification was very suitable, according to what was reported by the same authors, because every opal analysed through X-ray diffractometry could be included into one of these three groups. However, we must point out that Jones and Segnit (1971) did not include into the term of "opal" the materials of biogenic origin or the concretions (such as diatomites and geysersites) but assigned to these phases the term of "opaline silica."

According to Jones and Segnit (1971), the opals were classified as follows:

opal C: opal with a very ordered structure; the diffraction peaks in the X-ray pattern of α -cristobalite can be clearly identified even if accompanied by some weak peaks typical of tridymite and, in some cases, quartz.

opal CT: opal with a disordered structure; some diffraction peaks typical of α -cristobalite and α -tridymite in the X-ray pattern can be identified, the latter becoming more evident with an increase in disorder.

opal A: opal with a high disordered, almost amorphous, structure; only a diffuse band at about ~ 4.1 Å in the X-ray pattern can be identified.

The classification of Jones and Segnit (1971) subsequently underwent some small modifications. Some authors studied in more detail the sequence and disposition of the cristobalite/tridymite layers and the influence they could exert on the main diffraction peaks (Wilson *et al.*, 1974). Other authors subdivided opal A into two groups, namely, opal AN, amorphous opals with a pseudostructure similar to a glass (for instance, hyalite), and opal AG, amorphous opals with a pseudostructure similar to that of silica gel like, for instance, the noble opal. This subdivision was supported by analytical evidences and by the different origins of the two kinds of material. It is known that opal AN forms through deposition process, by the quenching of fluid phases at high temperatures on cold substrates, while opal AG forms through precipitation from aqueous solutions (Langer and Flörke, 1974).

In this paper we propose a new classification of opals through XRPD. This work was made possible because we had the possibility of accessing and analysing several samples collected from different worldwide areas. The analyses were carried out with two main purposes:

1. Identification of the crystallinity degree of opals, i.e., the degree of structural order/disorder of the minerals.
2. Identification of the eventual presence of accessory minerals in the samples.

Even XRPD is not commonly used in the field of gemology because it is a destructive technique, this review should be useful also to gemologists for the identification of common and noble opals.

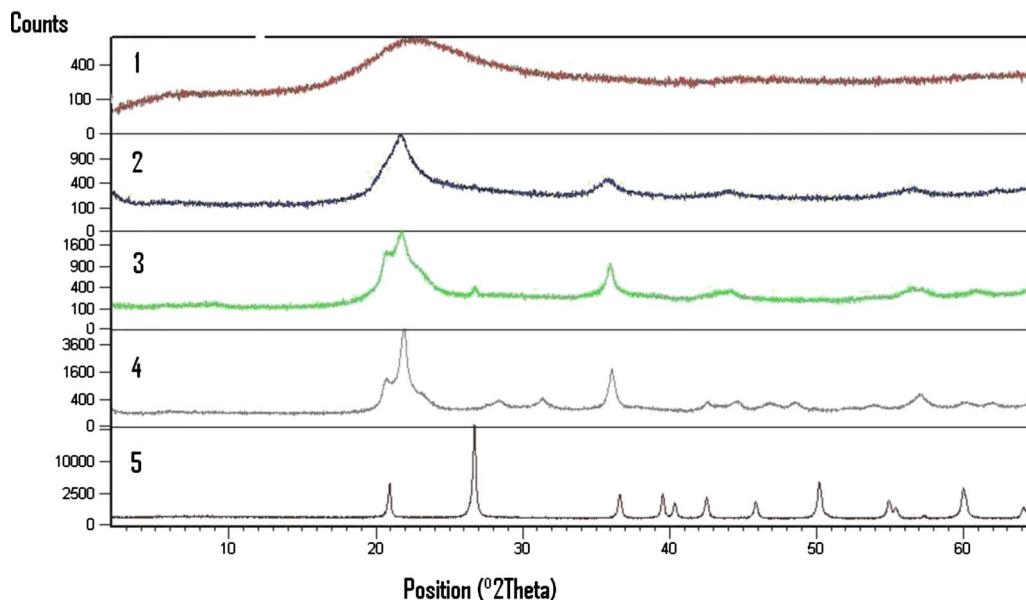


Figure 1. (Color online) XRPD patterns of opals analysed in this work: opal A (sample 1—light noble opal from Australia), disordered opal CT (sample 2—red fire opal from Australia), more ordered opal CT (sample 3—green opal bGW from Peru), opal C (sample 4—pink opal bVD from Peru), and quartz (sample 5—white chalcedony from Germany).

II. EXPERIMENTAL

A. Opal samples

About 75 samples of opal were analysed by XRPD: most come from Peru and others came from Tanzania, Brazil, Australia, Mexico, Madagascar, Slovakia, Italy, and Argentina. They mostly belong to the collection “Caucia-Ghisoli” (Ghisoli, 2008), while few other samples belonged to the collection of the museum “Don Bosco” of Torino (Italy). Further analyses were carried out on opals showing different colours and on some matrices. On the whole we carried out a total of 93 analyses. In particular, several differently coloured samples from Peru came from few centimeters thick veins in a copper ore in the area of Acari near Nazca, in the Arequipa Department, 600 km southeast of Lima (Ghisoli, 2008). Samples of crisopal came from the Hanety Hill, North of Dodoma, in the central part of Tanzania. Opals from Brazil came from the areas of Castelo do Piauí and of Varzea Grande in the state of Piauí. Other fire opals analysed in this work came from Western Australia, from the State of Queretaro in Mexico, and from the area around Bemia in the southeast of Madagascar. European white opals came from Slovakia and the Italian Alps and Italian hyalite came from Sardinia. Play colour opals came from the area of Lightning Ridge (Australia). Brown opal came from Patagonia (Argentina).

B. Specimen preparation

Opal samples were each manually grinded into an agate mortar and sieved to obtain a powder with a grain diameter $<33 \mu\text{m}$. Then, the powders have been pressed and mounted on the slab for the analyses.

C. Data collection

The XRPD analyses of samples of opal were carried out using a PW1800/10 Philips X-ray diffractometer, with a di-

vergent slit and a graphite diffracted-beam monochromator, operated at 40 kV and 40 mA with Cu $K\alpha$ radiation ($K\alpha_1 = 1.54060 \text{ \AA}$ and $K\alpha_2 = 1.54439 \text{ \AA}$). The speed and the angular range of the analyses were $0.02^\circ 2\theta/\text{s}$ and between 2° and $65^\circ 2\theta$, respectively.

The experimental XRPD data were analysed using the software X'PERT HIGH SCORE, V.2.0a (PANalytical). The phase identification of the XRPD results was done using the 1986 version of PDF database.

III. RESULTS AND DISCUSSION

A. Opal XRD patterns: Previous works

It is well known that the XRD patterns of opals do not have sharp diffraction peaks but show a broad and diffuse reflection at around $\sim 21.5^\circ 2\theta$ (see Figures 1 and 2). This broad peak was named, by some authors, with the term of “glass-peak” (Dódonoy and Takács, 1980) because of its resemblance with the diffuse peak produced by glass and merged with the background without interruptions. The corresponding value of d was frequently reported in literature (e.g., Giuseppetti and Veniale, 1969; Jones and Segnit, 1971; Sanders, 1975; Dódonoy and Takács, 1980; Morse and Casey, 1988; Herdianita *et al.*, 2000a; Herdianita *et al.*, 2000b) even if some authors reported d values between 4.01 and 3.88 Å (Garavelli, 1964) or between 4.1 and 3.8 Å (Kastner *et al.*, 1977). Also the “Gilson” opal is characterised by a broad peak centered at about $\sim 21.4^\circ 2\theta$ corresponding to a d value of $\sim 4.1 \text{ \AA}$, although this opal also shows accessory peaks related to well-crystallized cubic tetragonal zircon (Simonton *et al.*, 1986). Some authors also highlighted the presence of weak peaks corresponding to d values of about 2.0, 1.5, and 1.2 Å (Jones and Segnit, 1971; Rondeau *et al.*, 2004).

With regard to the opals showing a well-defined sequence of peaks (opal C), we considered at first the peaks typical of cristobalite and tridymite because these minerals

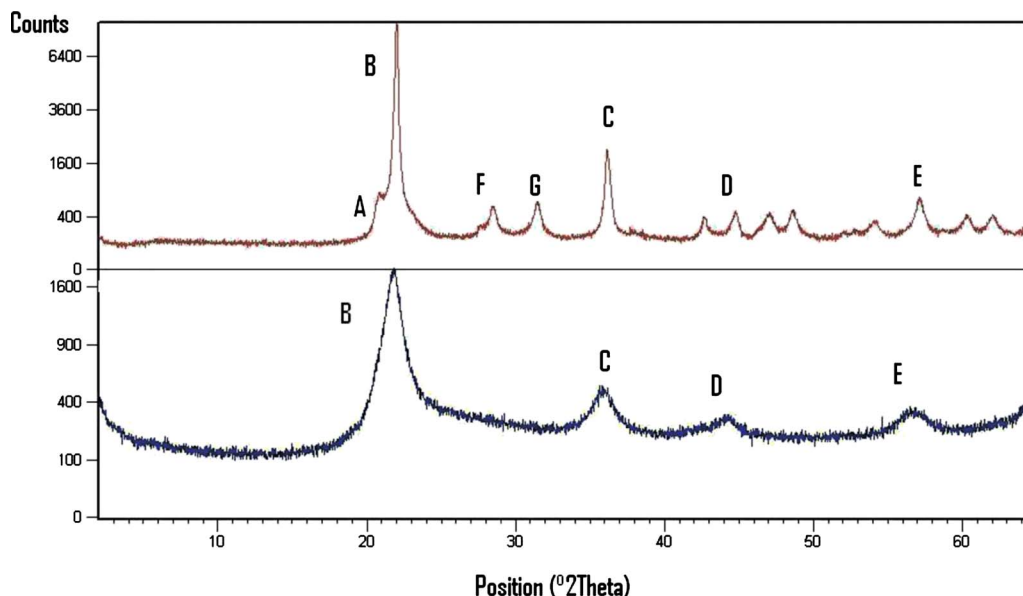


Figure 2. (Color online) Diagnostic peaks of opals (cristobalite/tridymite mixture): A, B, C, D, E and of cristobalite: F and G. The pattern of sample 1 is related to an orange fire opal from Mexico, while the pattern is of sample 2 to blue opal BVD from Peru.

mainly represent the crystalline component of opals. Successively, also the typical peak sequence of the sole well-crystallized α -cristobalite was considered. The diffraction peaks have been indicated with a capital letter. In particular, the peaks related to cristobalite/tridymite were named with the letters from A to E while those related to only cristobalite with the letters F and G (Figure 2).

As shown in Figures 1 and 2, the diffraction peaks indicating the presence of cristobalite/tridymite in opals can be described as follows:

Peak A: a “shoulder” at $\sim 20.65^\circ 2\theta$, corresponding to $d \sim 4.30$ Å. This is a weak peak diagnostic of tridymite, which can be presented along with the main peaks (q.v. B and C) (Flörke, 1955; 1967; Wilson *et al.*, 1974; Kastner *et al.*, 1977) and is probably related to the (040) plane of α -tridymite. This peak can be observed only in the opals with a quite ordered structure because it is masked by the background as the crystallographic disorder increases. Therefore, the intensity of this peak was reported to vary with the variation of the structural disorder (Flörke *et al.*, 1991). It also corresponds to the most intense peak of tridymite (Graetsch *et al.*, 1994), but it can also be diagnostic of α -cristobalite as is not present in the β phase (White *et al.*, 1988). Although this reflection is very evident in opal C, some authors considered it as the characteristic of opal CT (Jones and Segnit, 1971; Smith, 1997; Herdianita *et al.*, 2000a; Herdianita *et al.*, 2000b). While it generally features a d value of 4.3 Å (Flörke, 1967; Wilson *et al.*, 1974; Flörke *et al.*, 1991; Graetsch *et al.*, 1994), it can also show in opal-CT d values of 4.32 Å (Banergee and Wenzel, 1999), 4.318 to 4.300 Å (Bustillo *et al.*, 1999), 4.33 to 4.28 Å (Esenli *et al.*, 2003), 4.28 Å (Herdianita *et al.*, 2000a; Herdianita *et al.*, 2000b), and, lastly, 4.23 Å for the mixtures of the opal CT/A (Lynne and Campbell, 2004).

Peak B: a main peak at $\sim 21.80^\circ 2\theta$, with a d value of ~ 4.07 Å. It is the most important peak and corresponds to the combination of the reflections hkl (101) of α -cristobalite and hkl (-404) of α -tridymite (Flörke, 1955) or the hkl

(002) of the hexagonal polytype H of tridymite (Graetsch, 1994). It is frequently accompanied by the previously described shoulder A and can also show a secondary peak that can be very weak or also absent in opal C (Smith, 1998). The d values vary with the distance between the levels of tetrahedrons (Flörke *et al.*, 1991), and their shift allows us to define the degree of structural order in the opals, highlighting the gradual transition from opals CT to C (Kano, 1983; Graetsch *et al.*, 1994).

The d values of α -tridymite and α -cristobalite forming this peak are 4.107 and 4.04 Å, respectively; in opals the observed d values of this peak range depending from the authors: from 4.13 to 4.07 Å (De Jong *et al.*, 1987), from 4.12 to 4.07 Å (Herdianita *et al.*, 2000a; Herdianita *et al.*, 2000b), from 4.12 to 4.04 Å (Murata and Nakata, 1974; Graetsch, 1994; Graetsch *et al.*, 1994), from 4.11 to 4.04 Å (Jones and Segnit, 1971), from 4.11 to 4.03 Å (Elzea and Rice, 1996; Viti and Gemmi, 2006), and from 4.10 to 4.05 Å (Mizutani, 1977).

With regard to opal CT, the following d values for this peak were reported to range from 4.14 to 4.09 Å by Esenli *et al.* (2001, 2003), from 4.12 to 4.07 Å by Bustillo *et al.* (1999), from 4.11 to 4.06 Å by Cady *et al.* (1996), from 4.11 to 4.07 Å by Flörke *et al.* (1991), and from 4.10 to 4.07 Å by Elzea *et al.* (1994). The values of d for opal C were reported to range from 4.062 to 4.056 Å by Jones and Segnit (1971), from 4.06 to 4.05 Å by Flörke *et al.* (1991), from 4.055 to 4.036 Å by Esenli *et al.* (2001), and 4.05 Å by Bareille *et al.* (1990). After heating, the d value can decrease down to 4.025 Å (Jones and Segnit, 1971). This peak has also been reported as a variable single diffraction peak at around ~ 4.1 Å (Wilson *et al.*, 1974; Banergee and Wenzel, 1999) or as a peak characteristic of opal CT (Kastner *et al.*, 1977).

Peak C: a secondary peak at $\sim 36.05^\circ 2\theta$ corresponding to a d value of ~ 2.50 Å. Like the preceding one, this peak is also formed by a juxtaposition of two reflections, in particular the hkl (200) of α -cristobalite (Wilson *et al.*, 1974) and

the (341) of α -tridymite. It therefore derives from the sequence of stackings of the two phases (Flörke *et al.*, 1991).

This peak is the second with relevance in paracrystalline opals and is usually associated to the **B** peak and, sometimes, also to the **A** peak. This peak is also an indicator of the abundance of well-ordered cristobalite (Jones and Segnit, 1971) and is important for the identification of the degree of structural order in opals (Graetsch, 1994; Esenli *et al.*, 2001). According to some authors, this peak can be related to the presence of tridymite (Banergee and Wenzel, 1999) and is also reported as a “low-tridymite peak” in opal CT (Kastner *et al.*, 1977). Moreover, the variations of this peak were found to relate to the dimensions of the particles in opals (Guthrie *et al.*, 1995). It has a d value of 2.5 Å (Wilson *et al.*, 1974; Kastner *et al.*, 1977; Flörke *et al.*, 1991) but also of 2.51 Å (Banergee and Wenzel, 1999), of 2.485 Å (Viti and Gemmi, 2006), of 2.50 to 2.52 Å for the case of opal CT and 2.49 Å for opal C (Esenli *et al.*, 2001; 2003).

Peak D: a secondary peak at $\sim 44.50^\circ 2\theta$ corresponding to a d value of ~ 2.03 Å. It is a rather weak peak and is frequently ignored by many authors but sometimes can provide significant information on the structure of the opals (Guthrie *et al.*, 1995). It results from the juxtaposition of the values hkl (202) of α -cristobalite and of the (-432) of α -tridymite.

Peak E: a secondary peak at $\sim 56.85^\circ 2\theta$ corresponding to a d value of ~ 1.62 Å. This reflection is also rather weak and is usually ignored, but it can characterise the opals from some specific ores, such as the fire-coloured opals from Turkey (Esenli *et al.*, 2001). This peak corresponds to the juxtaposition of hkl (301) of α -cristobalite and (-513) of α -tridymite.

Peak F: a peak of a medium intensity at $\sim 28.50^\circ 2\theta$ corresponding to a d value of ~ 3.13 Å. It is consistent with the hkl (111) value of α -cristobalite. It was reported together with peak **G** by some authors (e.g., Jones and Segnit, 1971).

Peak G: a peak of medium intensity at $\sim 31.40^\circ 2\theta$ corresponding to a d value of ~ 2.84 Å. It matches the hkl value (102) of α -cristobalite (q.v. **F**).

Besides the previous peaks, some authors highlighted the occurrence of some other weak diffraction peaks, having d values of 4.48 Å (Jones and Segnit, 1971) and/or of 3.8 Å (Garavelli, 1964), which would indicate the presence of tridymite.

B. Opal XRD patterns: This work

The values relative to peaks **A** to **E** and **F** and **G** observed in the opals examined in this work are discussed in this section. Examples of the XRD patterns of the examined opals are reported in Figures 1 and 2, while the weighted means of the d values ($\langle d \rangle$) for each peak in the different typologies of opals are reported in Table I. Some diffraction peaks have not been detected because they were very weak or because they juxtaposed with those of other minerals (for instance, phyllosilicates). The abbreviation bVD and bGW are used to indicate materials with vitreous-dull and greasy-waxy lusters for the opals from Peru, respectively. Most results are in agreement with those in literature even if some are uncommon or also unpublished.

Shoulder **A** was observed in all the samples, with the

exception of some pink opals from Peru containing palygorskite and most fire opals, especially from Mexico. In any case, when detected, this diffraction showed a d value ranging from 4.340 to 4.263 Å ($\langle d \rangle = 4.301$ Å).

Peak **B** was detected in all the analysed opals and shows d values ranging from 4.114 to 4.017 Å ($\langle d \rangle = 4.073$ Å).

Peak **C** was observed in all samples. The d values of this diffraction peak range from 2.520 to 2.480 Å ($\langle d \rangle = 2.487$ Å).

Peak **D** was observed in all the samples, with the exception of some pink opals from Peru and some fire opals from Madagascar, which showed poorly defined XRD patterns. When detected, this diffraction peaks showed d values ranging from 2.071 and 2.017 Å ($\langle d \rangle = 2.041$ Å).

Peak **E** was observed in all the samples, with the exception of some bGW pink opals from Peru containing palygorskite, some fire opals from Madagascar that showed poorly defined XRD peaks. In the bGW pink opals, this diffraction peak is partly masked by the juxtaposition of the diffraction at $d = 1.6104$ Å due to enclosed palygorskite.

Diffraction peaks **F** and **G** were always observed together, forming a couple that is a characteristic of some specific categories, such as the bVD blue opals and bVD pink opals from Peru and blue opals from Brazil. These diffraction peaks were also observed in some samples of fire opals from Madagascar, from Brazil, and from Cuneo of Italy. As shown in Table I, peak **F** showed d values ranging from 3.140 to 3.121 Å ($\langle d \rangle = 3.130$ Å), while peak **G** had d values ranging from 2.851 to 2.832 Å ($\langle d \rangle = 2.841$ Å).

C. Accessory minerals present in opals of this work

The remaining diffraction peaks detected in our opals are generally related to some other accessory mineralogical phases. The most intense peaks are those of sepiolite, palygorskite, clay minerals, quartz, calcite, and gypsum. Regarding to palygorskite, this mineral can be recognised by its main reflection corresponding to $d_{100} \sim 10.4$ to 10.5 Å, which is partially embedded into the diffraction peak at 10 Å corresponding to illite. Other diagnostic diffraction peaks correspond to 6.44, 5.42, 4.49, 4.18, and 3.69 Å even if they are not always observable in the XRD patterns (Isphording, 1973; Chisholm, 1992). The presence of palygorskite was determined into 14 pink bGW samples of opals from Peru and into some related matrices. We also analysed the differently coloured parts of some samples and found that the different colour intensities are related to a relatively large presence of palygorskite, especially with respect to sepiolite.

Sepiolite has a diagnostic reflection with a corresponding d value of ~ 12 Å. Other reflections correspond to d values of 7.6, 5.0, 4.6, and 3.8 Å but can show variable intensities. Sepiolite was confidently detected only in four green and blue bGW samples from Peru. Some samples also feature the presence of clay minerals s.l., such as the bGW olive green opals from Peru, the green opals from Tanzania, the white opals from Italy, and the fire opals from Mexico and Madagascar.

The presence of α quartz was detected, in variable amounts, in 33 samples. In the bVD opals from Peru, which showed the presence of bands or coloured zones, the quartz is present in high amounts. Conversely, in the bGW olive

TABLE I. CT ratios, structural groups, d values of the diagnostic peaks of the opals analysed in this work. bVD=vitreous-dull luster; bGW=greasy-waxy luster.

Opal typology	d_A (Å)	d_B (Å)	d_C (Å)	d_D (Å)	d_E (Å)	d_F (Å)	d_G (Å)	CT ratio (%)	Structural group
Blue Peru (bVD)	4.29	4.04	2.49	2.03	1.62	3.13	2.84	C100 T0	C
Green and blue Peru (bGW)	4.29	4.08	2.50	2.05	1.64	C43 T57	CT
	4.32	4.11	2.50	2.05	1.62	C0 T100	CT
Olive green Peru (bGW)	4.31	4.06	2.50	2.06	1.63	C71 T29	CT
	4.30	4.08	2.50	2.05	1.63	C43 T57	CT
	4.30	4.07	2.49	2.05	1.63	C57 T43	CT
Pink Peru (bVD)	4.29	4.03	2.49	2.03	1.61	3.13	2.84	C100 T0	C
	4.30	4.05	2.47	2.03	1.61	3.14	2.85	C86 T14	C
Pink Peru (bGW)	4.32	4.10	2.51	C14 T86	CT
	...	4.08	2.49	C43 T57	CT
	...	4.06	2.49	2.04	C71 T29	CT
	...	4.09	2.50	C29 T71	CT
	4.31	4.07	2.49	C57 T43	CT
	4.31	4.11	2.50	2.05	C0 T100	CT
	4.30	4.09	2.51	2.04	1.63	C29 T71	CT
Brown Peru	4.29	4.07	2.49	2.05	C57 T43	CT
Yellow Peru	4.32	4.11	2.50	2.05	1.64	C0 T100	CT
Green Tanzania	4.31	4.10	2.50	2.05	1.63	C14 T86	CT
	4.30	4.09	2.50	2.05	1.64	C29 T71	CT
	4.26	4.02	2.48	2.02	1.61	3.12	2.84	C100T0	C
Blue Brazil	4.28	4.05	2.49	2.03	1.61	C86T14	C
Fire Brazil	4.31	4.04	2.48	2.02	1.61	3.13	2.84	C100T0	C
Fire Mexico	4.34	4.09	2.51	2.07	C29 T71	CT
	...	4.07	2.49	2.04	C57 T43	CT
	...	4.10	2.49	2.04	C14 T86	CT
Fire Australia	4.34	4.10	2.50	2.05	C14 T86	CT
	...	4.11	2.52	2.05	1.63	C0 T100	CT
	4.30	4.09	2.50	2.05	1.64	C29 T71	CT
White Slovakia	4.32	4.09	2.50	2.05	1.64	C29 T71	CT
	4.31	4.07	2.49	2.05	1.63	C57 T43	CT
	4.29	4.05	2.49	2.02	1.62	3.13	2.84	C86 T14	C
Fire Madagascar	4.27	4.02	2.48	...	1.61	3.12	2.84	C100 T0	C
	4.31	4.08	2.50	...	1.64	C43 T57	CT
	4.30	4.10	2.50	2.05	1.63	C14 T86	C
	4.28	4.11	2.50	2.05	1.63	C0 T100	CT
White Italy	4.30	4.03	2.49	2.02	1.61	3.14	2.85	C100 T0	C
Brown Italy	4.31	4.11	2.50	2.05	1.64	C0 T100	CT
Brown Argentina	4.29	4.08	2.49	2.05	C43 T57	CT

green and blue opals from Peru, the quartz is relatively low. In the other typologies of samples, quartz generally occurs only as an accessory phase but is slightly higher in some opals from Patagonia.

D. Discussion

The XRD analyses carried out in this work revealed that the structure of six of the samples of opal is completely amorphous, while α -cristobalite and α -tridymite (crystalline phases) are abundant in 63 samples. Several samples of opals are paracrystalline and characterised by a variably ordered structure due to the intercalation of cristobalite and tridymite layers (Graetsch, 1994). Consequently, we were able to recognise all the different typologies of opals (A, CT, and C as shown in Figure 1) with their related “intermediate crystallization” (Jones and Segnit, 1971). In several samples, vari-

able quantities of accessory phases such as palygorskite, sepiolite, clay s.l., α quartz, and, in few cases, calcite and gypsum were identified.

Concerning the amorphous opals, in three samples it was not possible to identify significant diffraction peaks, while other three samples showed the characteristic broad and diffuse band (at about 4.1 Å) typical of the amorphous opals (see Figures 1 and 2).

On the contrary, the paracrystalline opals showed intense diffraction peaks. The intensity is not probably related to the amount of cristobalite but to the degree of order of the opal. The variably amorphous structure of the opals becomes progressively more ordered during the diagenetic process (Juchem *et al.*, 2004; Lynne and Campbell, 2004). According to some authors, the tridymite in the opals also shows a similar behaviour, transforming into α -cristobalite (Graetsch, 1994). With the increasing of the diagenetic process, the de-

gree or order increases following the sequence opal-A → opal-CT → opal-C → chalcedony → quartz. In this sequence the transition from opal CT to opal C takes place gradually and slowly, as it mostly consists in a transformation of tridymite into cristobalite. However, it seems that in some siliceous volcanic deposits, the opals C and CT may form directly *in situ* without following the previous sequence (Graetsch *et al.*, 1994).

Discriminating the paracrystalline opals (C and CT opals) from the opals A through XRD is relatively easy, while it is more difficult to discriminate the opals C and CT. Probably, the opals C and CT represent a continuous series of intergrowths among the stacking sequences of the end members cristobalite and tridymite (Elzea and Rice, 1996). As a consequence, the local order increases with the decreasing of the disordered layers, so that the passage from opals CT to C can take place through intermediate steps (Graetsch *et al.*, 1994).

Cristobalite in natural environment shows two different structural forms of low and high temperatures: tetragonal α -cristobalite and cubic β -cristobalite, respectively. In the opals, as previously mentioned, cristobalite is nearly exclusively represented by the low-temperature phase. Differently, tridymite in natural environment presents low-temperature and a high-temperature forms, α -tridymite and β -tridymite, respectively. The low-temperature phase can be monoclinic and orthorhombic. The high-temperature phase is hexagonal and presents several polytypes, but the most common are the 10H and the 20H. A large part of the previous forms of tridymite can be present in the opals, but their identification and quantification through XRD are difficult. The investigations on the structure of the different forms of tridymite are still not conclusive even if interesting studies on this topic are present in literature (e.g., Graetsch and Flörke, 1991).

For the aims of our work it was necessary to define a parameter to evaluate the degree of order/disorder in the opals C and CT, which is related to the “content” of cristobalite/tridymite. The parameter is represented by the shift of the main peak **B**, which has already been used successfully by several authors. Peak **B** is the most important reflection and always detectable. It can indicate the different arrangements of tetrahedrons in the sequence of stackings of cristobalite and tridymite. According with the previously cited works, we considered the value d of 4.11 Å as diagnostic of tridymite and the value of 4.04 Å as diagnostic of cristobalite. The ratio between the amounts of tridymite and cristobalite in the crystalline fraction of the opals can be defined as

$$\begin{aligned} C/T_{\text{XRPD}} &= (d_{\text{Tryd}} - d_{\text{measured}})/(d_{\text{Tryd}} - d_{\text{Crist}}) \\ &= (4.11 \text{ \AA} - d_{\text{measured}})/(4.11 \text{ \AA} - 4.04 \text{ \AA}). \end{aligned} \quad (1)$$

The calculated values of C/T for the analysed opals are reported in Table I.

The value of 4.11 Å is considered to be ideal for d_{Tryd} , assuming that all the tridymite is present as the monoclinic low-temperature phase. Also in the case that the polytype 20H of the high-temperature phase was present, then the diffraction peak at 4.11 Å would combine with the 20H diffraction peak at 4.075 Å. This peak is due to the diffraction d_{100} at 4.27 Å that causes a decreasing of the d values of shoulder **A**.

Once the values of C/T were determined for all the analysed samples, it was necessary to find a criterion that goes beyond a numerical value, which can be influenced by a different degree of disorder in a particular zone of a sample. Previous works in literature did not define a univocal way to separate opal-C values d_{100} and opal CT. Therefore, on the basis of the collected results, we try to advance a new proposal. In particular, we establish that the d value of the **B** peak (d_{B}) corresponding to 4.05 Å is the limit for opal C. Consequently, one deduces that the opals that show values $d_{\text{B}} \geq 4.06$ Å must be classified as opal CT. This differentiation is strictly related to the presence or absence of the two **F** and **G** peaks at $\sim 30^\circ 2\theta$, typical for α -cristobalite. However, the limit at 4.06 Å for opal C can have some exceptions because of the degree of order/disorder. There are opals that show poorly defined diffraction patterns that make hard to identify the **F** and **G** peaks even if they show the d value of 4.06 Å (see Table I). On the contrary, the d value of 4.06 Å and a shaper XRD pattern for opals, these two peaks, diagnostic of α -cristobalite, are evident. Nevertheless, we must point out that most of samples showed XRD patterns that supported the previous consideration.

Once the general parameter is defined, some considerations concerning the behaviour of other diffraction peaks can be discussed in order to estimate the validity of the above assumed criterion.

The diffraction peaks **A**, **B**, and **C** are characterised by variable shifts. The d values of the different opal groups, related to the 2θ angular position, increase with increasing structural disorder (see Table I). Particularly, the diffraction peaks **D** and **E**, which show more shifts, evidence this behaviour as they separate more clearly the two types of opal (see Table I). The only data that yielded slightly different results are those relative to shoulder **A**. As previously reported, this peak is characteristic of the presence of tridymite. It is, therefore, likely that this value depends on the relative proportion of the different polytypes of tridymite. The group of fire opals of Madagascar (see Table I) presents a great heterogeneity: a group is formed nearly exclusively by α -cristobalite bearing opals, while another group features high contents of α -tridymite. The structural difference of these opals is probably related to the various unknown origins of these materials.

In addition of peaks **F** and **G** for opal C, other peaks are also present at the angular positions of $\sim 42.5^\circ$, 47° , 48° , 5° , 54° , 60° , and $62^\circ 2\theta$. However, these diffraction peaks were not considered, but for a confirmation, because their intensities are small and often not evident due to the general structural disorder. In addition, α -cristobalite has other additional 15 diffraction peaks, but they are not in the 2θ range used in this study. These diffraction peaks have d values ranging from 1.398 to 1.183 Å and are very weak. In opal CT we mostly observe a general and increasing trend to a broadening of peaks **B** and **D**, accompanied by a progressive fading of shoulder **A** and an increasing of the disorder of the entire diffraction pattern.

Some values of peak **B** showed values of $d < 4.04$ Å; in particular, some pink bVD opals from Peru and one opal from Italy showed d values of ~ 4.03 Å and blue opals from Brazil and fire opals from Madagascar showed d values of ~ 4.02 Å. It is known that, under heating, opal may convert

into well-ordered forms of cristobalite (Wahl *et al.* 1961). In addition, Jones and Segnit (1971) heated some opal CT having d values of 4.114 Å up to temperatures of 1150 and 1300 °C and observed that the d values decreased to 4.038 and 4.025 Å, respectively. Therefore, we can hypothesise that our opals, which were extracted in volcanic settings, underwent a natural heating process that caused the decreasing of their d_B values.

On the other hand, in our samples we have never found d values higher than 4.114 Å, such as $d=4.127$ Å reported for fire opals from Turkey by Esenli *et al.* (2001).

For a correct identification of opal, it would be important to identify a correct d value that allows the differentiation between opal CT and opal T. This limit could be the d value of 4.10 Å. However, because of the high disorder of the structure, other secondary peaks that can confirm the previous differentiation are frequently weak or not observable. For this reason, in according with other authors (e.g., Elzea and Rice, 1996), we will consider the opals with d values higher than 4.10 Å to be high disordered opal CT but not opal T.

The accessory minerals that can characterise the different typologies of opals turn out to be sepiolite and palygorskite. Palygorskite and especially sepiolite are also very rich in silica. Therefore, they can also form in the same silica rich environments where opals form.

Sepiolite and palygorskite have never been found together in the opals analysed in this work, which is different from what was reported by other authors on similar opals from Peru (Brajkovic *et al.*, 2007). These minerals have been used as markers of particular typologies of opals. For instance, orthorhombic sepiolite was found only in blue and green bGW opals from Peru, although in modest amount and less frequently than palygorskite. Monocline palygorskite, on the contrary, was exclusively found in the pink bGW opals from Peru, in particular into the pink, white, and yellow parts. A large amount of palygorskite frequently occurs in opal; this is in agreement with reported palygorskite contents up to around 40% (Brajkovic *et al.*, 2007; Fritsch *et al.*, 2004). The amount of palygorskite present in opal appears proportional to the saturation of their colour, as can be deduced by the strong differences in intensities in various coloured parts of a same sample; this is due to the presence of organic colourings absorbed into palygorskite that could also be the cause of the pink colour. Similarly, in the crusts that cover coarse samples, palygorskite is sometimes associated with zeolites: stilbite and barrerite (Brajkovic *et al.*, 2007). Different from sepiolite and palygorskite, clay minerals in the samples analysed in this work do not seem relevant for the determination of the colour, as observed, for instance, in the red opals from Macedonia (Bermanec *et al.*, 2004).

In a few cases the presence of α quartz can provide some information for the characterisation of the opals. Conversely, calcite occurs only in trace and cannot be used for the previous purposes.

IV. CONCLUDING REMARKS

The purposes of this work are as follows:

1. Drawing up a detailed review of the application of XRD analysis on opals.

2. Describing the most important results of XRD analyses in literature and compare them with the new data of the analyses obtained from opals extracted from ores worldwide.
3. Proposing of a simple method to classify the opals based on their degrees of order/disorder and to discriminate opal C from opal CT.

Based on the XRD analyses, it is concluded that the original methods for the identification of different kinds of opals (namely, A, CT, and C) based on the XRPD technique previously reported in literature by Jones and Segnit (1971) and Elzea and Rice (1996) are still valid. These three types of opal can be easily identified based on their XRPD patterns. In particular, opal C is characterised by a peak corresponding to a d value between 4.02 and 4.05 Å and by the presence of two other peaks at 3.13 and 2.84 Å. Opal CT shows only a peak corresponding to a d value ranging from ~4.06 to 4.11 Å. Also, it is not possible to distinguish an opal CT from a theoretical opal T (in this work, $d=4.11$ Å) as previously reported by Elzea and Rice (1996). As a matter of fact, cristobalite crystallites are stacked in a tridymite superstructure. Hence, a single silica molecule can be considered as a part of a cristobalite crystal in one direction and a tridymite crystal in another direction.

Regarding to the accessory minerals, palygorskite and sepiolite are particularly important for the colour of opals. For instance, the opals from Acari Mine of Peru are characterised by the presence of palygorskite and sepiolite with a greasy-waxy luster. On the other hand, the opals with a vitreous-dull luster obtained from Lily Maine of Peru contain neither palygorskite nor sepiolite.

- Baier, E. (1932). "Die optik der edelopale," *Z. Kristallogr.* **81**, 183–218.
- Banergee, A. and Wenzel, T. (1999). "Black opal from Honduras," *Eur. J. Mineral.* **11**, 401–408.
- Barelle, G., Labracherie, M., Maillat, N., and Latouche, C. (1990). "Quantification des teneurs en opale biogène des sédiments de l'Océan Austral par diffractométrie X," *Clay Miner.* **25**, 363–373.
- Bermanec, V., Tomašić, N., Karfunkel, J., Scholz, R., Kniewald, G., and Jaksch, H. (2004). *Applied Mineralogy*, edited by M. Pecchio, F. R. Dias de Andrade, L. Z. D'Agostino, H. Kahn, L. M. Sant'Agostino, and M. M. Lé Tassinari (ICAM-BR, São Paulo), pp. 525–527.
- Brajkovic, A., Rolandi, V., Vignola, P., and Grizzetti, R. (2007). "Blue and pink opals from Acari, Peru. Their optical, structural and spectroscopic features," *The Aust. Gemmol.* **23**, 3–15.
- Bustillo, M. A., García, R., and García Pérez, M. V. (1999). "Estados estructurales del opalo CT en rocas opalinas sedimentarias e hidrotermales," *Bol. Soc. Española Mineral.* **22-A**, 21–22.
- Cady, S. L., Wenk, H. R., and Downing, K. H. (1996). "HRTEM of microcrystalline opal in chert and porcelanite from the Monterey Formation, California," *Am. Mineral.* **81**, 1380–1395.
- Chisholm, J. E. (1992). "Powder-diffraction patterns and structural models for palygorskite," *Can. Mineral.* **30**, 61–73.
- Cirilli, V. and Giannone, A. (1941). "Sulla presenza di β -e α -cristobalite in alcuni campioni di opale," *Rend. Accad. Sci. Fis. Mat., Naples* **11**, 99–104.
- De Jong, B. H. W. S., Van Hoek, J., Veeman, W. S., and Manson, D. V. (1987). "X-ray diffraction and ^{29}Si magic-angle-spinning nmr of opals: Incoherent long- and short-range order in opal-CT," *Am. Mineral.* **72**, 1195–1203.
- Dódony, I. and Takács, J. (1980). "Structures of precious opal from Červenica," *Ann. Univ. Sci. Budap. Rolando Eotvos Nominatae, Sect. Geol.* **22**, 37–50.
- Dwyer, F. P. and Mellor, D. P. (1932). "A note on the occurrence of β -cristobalite in Australian opals," *J. Proc. R. Soc. N. S. W.* **66**, 378–382.
- Dwyer, F. P. and Mellor, D. P. (1934). "An X-ray study of opals," *J. Proc. R.*

- Soc. N. S. W. **68**, 47–50.
- Elzea, J. M., Odom, I. E., and Miles, W. J. (1994). "Distinguishing well ordered opal-CT and opal-C from high temperature cristobalite by x-ray diffraction," *Anal. Chim. Acta* **286**, 107–116.
- Elzea, J. M. and Rice, S. B. (1996). "TEM and X-ray diffraction evidence for cristobalite and tridymite stacking sequences in opal," *Clays Clay Miner.* **44**, 492–500.
- Esenli, F., Kumbasar, I., Eren, R. E., and Uz, B. (2001). "Characteristics of opals from Simav, Turkey," *Neues Jahrb. Mineral., Monatsh.* **2001**, 97–113.
- Esenli, F., Kumbasar, I., Esenli, V., and Kirikoğlu, S. (2003). "A study on the characteristics of some opals from Turkey," *Neues Jahrb. Mineral., Monatsh.* **2003**, 177–192.
- Fenoglio, M. and Sanero, E. (1943). "Sulla presenza e diffusione della cristobalite β negli opali dei giacimenti di magnesite delle Prealpi Piemontesi," *Atti Accad. Sci. Torino, Cl. Sci. Fis., Mat. Nat.* **78**, 265–273.
- Flörke, O. W. (1955). "Zur frage des "hoch-cristobalit" in opalen bentoniten und gläsern," *Neues Jahrb. Mineral., Monatsh.* **1955**, 217–224.
- Flörke, O. W. (1967). "Die modificationen von SiO_2 ," *Fortschr. Mineral.* **44**, 181–230.
- Flörke, O. W., Graetsch, H., Martin, B., Röller, K., and Wirth, R. (1991). "Nomenclature of micro-and non-crystalline silica minerals, based on structure and microstructure," *Neues Jahrb. Mineral., Abh.* **163**, 19–42.
- Fritsch, E., Gaillou, E., Ostroumov, M., Rondeau, B., Devouard, B., and Barreau, A. (2004). "Relationship between nanostructure and optical absorption in fibrous pink opals from Mexico and Peru," *Eur. J. Mineral.* **16**, 743–751.
- Fronde, C. (1962). *The System of Mineralogy of James Dwight Dana and Edward Salisbury Dana Yale University 1837–1892*, 7th ed. (Wiley, New York), Vol. III.
- Garavelli, C. L. (1964). "Ordine e disordine negli opali," *Atti Soc. Toscana Sci. Nat. Pisa Mem., Ser. A* **71**, 133–186.
- Ghisoli, C. (2008). "Opals: Characterization nomenclature definition and proposal of a new varieties classification following the discovery of new materials in Peru," *Sci. Acta* **2**, 27–34.
- Giuseppetti, G. and Veniale, F. (1969). "Relazioni tra natura dell'acqua, morfologia e struttura degli opali: Nota II," *Rend. Soc. Ital. Mineral. Petrol.* **25**, 407–437.
- Graetsch, H. (1994). "Structural characteristics of opaline and microcrystalline silica minerals," *Rev. Mineral.* **29**, 209–232.
- Graetsch, H. and Flörke, O. W. (1991). "X-ray powder diffraction patterns and phase relationships of tridymite modifications," *Z. Kristallogr.* **195**, 31–48.
- Graetsch, H., Gies, H., and Topalovic, I. (1994). "NMR, XRD and IR study on microcrystalline opals," *Phys. Chem. Miner.* **21**, 166–175.
- Greig, J. W. (1932). "The existence of the high-temperature form of cristobalite at room temperature and the crystallinity of opal," *J. Am. Chem. Soc.* **54**, 2846–2849.
- Guthrie, G. D., Jr., Bish, D. C., and Reynolds, R. C., Jr. (1995). "Modeling the X-ray diffraction pattern of opal-CT," *Am. Mineral.* **80**, 869–872.
- Herdianita, N. R., Browne, P. R. L., Rodgers, K. A., and Campbell, K. A. (2000a). "Mineralogical and textural changes accompanying ageing of silica sinter," *Miner. Deposita* **35**, 48–62.
- Herdianita, N. R., Rodgers, K. A., and Browne, P. R. L. (2000b). "Routine instrumental procedures to characterise the mineralogy of modern and ancient silica sinters," *Geothermics* **29**, 65–81.
- Ishphording, W. C. (1973). "Discussion of the occurrence and origin of sedimentary palygorskite-sepiolite deposits," *Clays Clay Miner.* **21**, 391–401.
- Jones, J. B., Sanders, J. V., and Segnit, E. R. (1964). "Structure of opal," *Nature (London)* **204**, 990–991.
- Jones, J. B. and Segnit, E. R. (1971). "The nature of opal: I. Nomenclature and constituent phases," *J. Geol. Soc. Aust.* **18**, 57–68.
- Jones, J. B., Segnit, E. R., and Nickson, N. M. (1963). "Differential thermal and X-ray analysis of opal," *Nature (London)* **198**, 1191.
- Juchem, P. L., Lubachesky, R., De Brum, T. M. M., and Waichel, B. L. (2004). in *Applied Mineralogy*, edited by M. Pecchio, F. R. Dias de Andrade, L. Z. D'Agostino, H. Kahn, L. M. Sant'Agostino, and M. M. M. Lé Tassinari (ICAM-BR, São Paulo), pp. 559–562.
- Kano, K. (1983). "Ordering of opal-CT in diagenesis," *Geochem. J.* **17**, 87–93.
- Kastner, M., Keene, J. B., and Gieskes, J. M. (1977). "Diagenesis of siliceous oozes: I. Chemical controls on the rate of opal-A to opal-CT transformations: An experimental study," *Geochim. Cosmochim. Acta* **41**, 1041–1059.
- Kerr, P. F. (1924). "The determination of opaque ore minerals by X-ray diffraction patterns," *Econ. Geol.* **19**, 1–34.
- Langer, K. and Flörke, O. W. (1974). "Near infrared absorption spectra (4000–9000 cm^{-1}) of opals and the role of "water" in these $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ minerals," *Fortschr. Mineral.* **52**, 17–51.
- Laves, F. (1939). "Über den einfluss von spannungen auf die regelung von quartz- und cristobalit in chaledon, quartzin, und lussatit," *Naturwiss.* **27**, 705–707.
- Levin, I. and Ott, E. (1932). "The crystallinity of opals and the existence of high-temperature cristobalite at room temperature," *J. Am. Chem. Soc.* **54**, 828–829.
- Levin, I. and Ott, E. (1933). "X-ray study of opals, silica glass and silica gel," *Z. Kristallogr.* **85**, 305–318.
- Lynne, B. Y. and Campbell, K. A. (2004). "Morphologic and mineralogic transitions from opal-A to opal-CT in low-temperature siliceous sinter diagenesis, Taupo volcanic zone, New Zealand," *J. Sediment Res.* **74**, 561–579.
- Mitchell, R. S. and Tufts, S. (1973). "Wood opal: a tridymite-like mineral," *Am. Mineral.* **58**, 717–720.
- Mizutani, S. (1977). "Progressive ordering of cristobalitic silica in the early stage of diagenesis," *Contrib. Mineral. Petrol.* **61**, 129–140.
- Morse, J. W. and Casey, W. H. (1988). "Ostwald processes and mineral paragenesis in sediments," *Am. Sci.* **288**, 537–560.
- Murata, K. I. and Nakata, K. (1974). "Cristobalitic stage in the diagenesis of diatomaceous shale," *Science* **184**, 567–568.
- Raman, C. V. and Jayaraman, A. (1953). "The structure of opal and the origin of its iridescence," *Proc. Natl. Inst. Sci. India* **38**, 101–108.
- Rinne, F. (1924). "III. Röntgenographische untersuchungen an einigen feinzerteilten mineralien, kunstprodukten und dichten gesteinen," *Z. Kristallogr.* **60**, 55–69.
- Rondeau, B., Fritsch, E., Guiraud, M., and Renac, C. (2004). "Opals from Slovakia ("Hungarian" opals): A re-assessment of the conditions of formation," *Eur. J. Mineral.* **16**, 789–799.
- Sanders, J. V. (1975). "Microstructure and crystallinity of gem opals," *Am. Mineral.* **60**, 749–757.
- Simonton, T. C., Rustum, R., Komarneni, S., and Breval, E. (1986). "Microstructure and mechanical properties of synthetic opal: A chemically bonded ceramic," *J. Mater. Res.* **1**, 667–674.
- Smith, D. K. (1997). "Evaluation of the detectability and quantification of respirable crystalline silica by X-ray powder diffraction methods," *Powder Diffr.* **12**, 200–227.
- Smith, D. K. (1998). "Opal, cristobalite and tridymite: Noncrystallinity versus crystallinity, nomenclature of the silica minerals and bibliography," *Powder Diffr.* **13**, 2–19.
- Sosman, R. B. (1932). "The inversion of cristobalite," *J. Am. Chem. Soc.* **54**, 3015.
- Taliaferro, N. L. (1935). "Some properties of opal," *Am. J. Sci.* **30**, 450–474.
- Viti, C. and Gemmi, M. (2006). "Micronanotessitura, cristallinità e composizione di opali naturali e sintetici," *Riassunto dell'Intervento all'85° Congresso SIMP-Fluminimaggiore*, (I), 27–30.
- Wahl, F. M., Grim, R. E., and Graf, R. B. (1961). "Phase transformations in silica as examined by continuous X-ray diffraction," *Am. Mineral.* **46**, 196–208.
- White, D. E., Hutchinson, R. A., and Keith, T. E. C. (1988). "The geology and remarkable thermal activity of Norris Geyser Basin, Yellowstone National Park, Wyoming," U.S. Geological Survey Professional Paper No. 1456, 1–8.
- Wilm, D., Hofmann, U., and Endell, K. (1934). "Über die bedeutung von röntgeninterferenz-untersuchungen bei hohen temperaturen für die keramische forschung," *Sprechsaal Keram.-Glas-Email* **38**, 1–8.
- Wilson, M. J., Russell, J. D., and Tait, J. M. (1974). "A new interpretation of the structure of disordered α -cristobalite," *Contrib. Mineral. Petrol.* **47**, 1–6.