



OPAL FROM QUERÉTARO, MEXICO: FLUID INCLUSION STUDY

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The distinctive orange-to-red "fire" opals from Querétaro have not been found in significant quantities at any other locality. Through modern analytical methods, it has been determined that these opals formed at about 160°C, from hydrous silica gels contained in fluids with small (up to 10%), variable amounts of NaCl and CO₂. These data, combined with geologic data, help explain the rare occurrence of this type of rhyolitic opal deposit.

The Querétaro area, about 200 km northwest of Mexico City, has produced distinctive gem-quality opals for at least a hundred years. These opals occur in cavities and fractures within rhyolitic lava flows and are mined in open pits. They are unique among opals because of their unusual orange to red color and translucent to transparent diaphaneity (figure 1), unusually low refractive index (1.42–1.43, to as low as 1.37), and distinctive inclusions (see Koivula et al., 1983). They also represent the only significant amounts of gem-quality opal known to occur in a rhyolite. To date, however, little research has been conducted into the nature of the geologic environment that produced these unique stones.

Important clues to the geologic conditions that created a particular gem material can be found in its inclusions. Koivula et al. (1983) and Gübelin (1985,

1986) provide the only detailed investigations of inclusions in the opals from Querétaro. They report three-phase (rare), two-phase, and single-phase inclusions. Mineral inclusions identified by X-ray diffraction are hornblende (some altered to limonite), goethite, hematite, fluorite, quartz, cristobalite, and chalcedony. Kaolinite was tentatively identified by X-ray diffraction, and pyrite was identified visually. Several inclusions in opals from this area are also illustrated in Gübelin and Koivula (1986).

However, there has been no attempt to study the chemical compositions of the fluids and gases in the inclusions. Further, other than generalized statements to the effect that Mexican opals must have formed at high temperatures because they are in volcanic (lava) rocks (see, e.g., Gübelin, 1986), there has been no attempt to quantify their temperature of formation. We do know that Australian opals form at low temperatures from circulating groundwaters and are found in sedimentary environments (see, e.g., Keller, 1990).

The modern methods of *microthermometry* and *mass spectrometry* are ideally suited to obtain data that can be used to determine the composition of fluid and gas inclusions, and the temperature of formation of the host minerals. (Please see the "Glossary" for definitions of these and other technical terms indicated by italics in this article.) The authors have applied these methods to analyze fluid inclusions in these Mexican opals and thus gain a better understanding of their mode of formation.

ABOUT THE AUTHORS

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Figure 1. One of the most distinctive gem opals is the orange to red "fire" opal found in the area of Querétaro, Mexico. Here, cabochons of this material have been set—with rutilated quartz, agate, and sapphire—into an unusual pendant-and-earrings combination designed by Paula Kreviche. Courtesy of Paula Kreviche; photo © Harold & Erica Van Pelt.

BACKGROUND

Fluid inclusions contain droplets of the mineral's nurturing environment that were caught in defects or other "traps" on the crystal surface during growth (Roedder, 1984). These features are frequently called "voids" in the gemological literature, but liquids usually fill these "voids" completely as long as the mineral remains at the elevated temperatures present during formation. Then, as the liquid cools and contracts, a tiny gas bubble may form in the space made available by the smaller volume of the cool liquid; this is frequently seen in quartz, Sri Lankan sapphires, and Colombian emeralds, among others. By gently heating a mineral until the gas is reabsorbed into the expanding liquid, we can establish the temperature at which the mineral grew, that is, the *homogenization temperature*. Further, if the fluid is solidified by freezing, we can estimate the chemical composition of

the fluid by determining: (a) the temperature at which the fluid freezes, and (b) the *melting point of the fluid*. The composition of gases trapped in fluid inclusions can be ascertained by opening the fluid inclusions under vacuum (by breaking the specimen) and then introducing the released gases into a *mass spectrometer*.

EXPERIMENTAL METHODS

Several thousand tumble-polished opals were inspected with the microscope, but only a few were found suitable for the studies contemplated. These studies included:

- A. The slow, carefully controlled heating of four samples containing liquid-gas inclusions. A Fluid Inc. heating/freezing stage (figure 2) was used to determine the homogenization tem-



Figure 2. Microthermometric experiments were conducted using this heating-freezing stage (thin, brown in color; see arrow), which was set up on a petrographic microscope. This instrument allows the researcher to observe changes in the fluid inclusion as it is exposed to different temperatures—which are displayed on the right (23.1°C in this case)—at any moment during an experiment.

GLOSSARY

Clathrate A solid containing water and a gas, which in this case is H₂O plus CO₂. These are stable only at low temperatures (the maximum temperature at which any solid CO₂ clathrate is stable is about +10°C).

Decrepitation When a mineral, such as opal, “breaks up” (fractures) on heating.

Eutectic temperature The lowest possible melting point in a multi-component (e.g., H₂O-NaCl) system.

Homogenization temperature The temperature at which primary liquid-and-gas inclusions become a single phase, which is assumed to be equivalent to the host’s temperature of formation.

Mass spectrometer An instrument designed to measure the *molecular mass* of a gas (on the basis of which its composition can be determined).

Melting point of fluids The point at which a liquid that has been solidified by freezing (such as ice), melts when it is heated.

Microthermometry Observation under the microscope of changes caused by temperature variations.

Molecular mass The weight of one mole of a molecule. For water, H₂O mass = 18.

Phase separation The process by which two phases form from one; e.g., a CO₂-rich gas plus an aqueous liquid form from a single fluid state that contains both.

Reversible (equilibrium) A chemical/physical reaction that can be caused to change direction by a small change in temperature.

Saline Containing any dissolved salt, such as sodium chloride (NaCl).

Supercooled liquid A liquid that remains liquid below its normal solidification temperature, e.g., water that remains liquid below 0°C.

perature (assumed to be equivalent to the temperature of formation of the opal host).

B. Melting-point studies of the fluids from three of the above samples, and of certain crystals that form at freezing temperatures, to estimate the chemical compositions of the fluids.

C. Mass spectrometry of released gases from 30 samples to determine the compositions of the gases (figure 3).

Mass spectra were obtained at room temperature. The opals were placed under vacuum, and several background scans were made. The mass spectrometer was then set to scan when a pressure burst from the release of a gas was detected. To release the gases trapped in the fluid inclusions, we lifted ball bearings with a magnet and then dropped them on the samples. A *molecular mass* range of 1 to 125 was scanned at 3 milliseconds per mass unit.

RESULTS

Observations with the Microscope. Most of the fluid inclusions in the Mexican opals studied here contained a single fluid or a fluid plus a solid (see, e.g., figure 4). To determine the nature of these inclusions, we attempted to induce the formation of a gas phase by “stretching”—that is, we heated the samples to build pressure within the fluid inclusions in order to “stretch” the enclosing solid (samples were heated to the point where they began to fracture and break apart, about 160°C). However, no gas phase formed on cooling of the inclusions to room temperature. If these fluid inclusions had been composed of water, this heating would have produced a stretching of the

host opal as the water expanded, as occurs in aqueous inclusions in other minerals such as quartz and calcite. From the failure of the heating procedure to stretch the opal, we concluded that most of the fluid inclusions in Mexican opals (again, see figure 4) are composed of a gel rather than a liquid. To confirm our findings, we also cooled the samples to -120°C . Similarly, we observed no changes.

Because these types of inclusions do not provide the information needed to analyze the temperature and composition of the original mineral-forming solutions, we subsequently limited our investigation to those fluid inclusions in which a gas was evident.

Of the four samples in which we had identified aqueous liquid-gas inclusions, one particularly useful specimen contained numerous liquid-gas (vapor) inclusions as well as liquid-solid and liquid-solid-gas inclusions. An overall view of this Mexican opal,

Figure 3. This mass spectrometer (a quadrupole type) was used to determine the composition of the gases released from the opals. The arrow points to the chamber in which the sample is placed. Gases released from the sample pass through the glass tubing into the mass spectrometer for analysis.

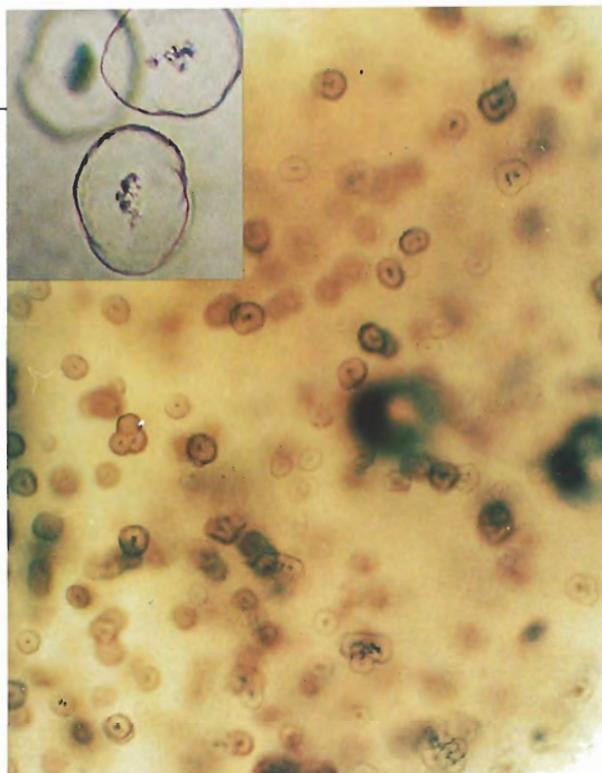
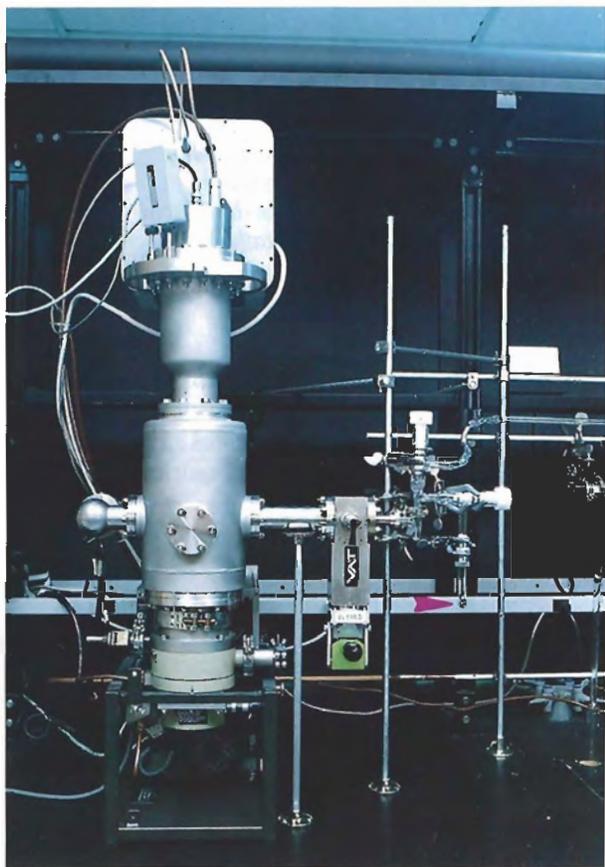


Figure 4. These fluid and fluid-solid inclusions are typical of those observed in the thousands of Mexican opals examined. The major portion of the photograph was taken at $50\times$; the inset, at $580\times$.

which is about 1 cm in longest dimension, is shown in figure 5 (bottom center). The locations of selected fluid inclusions (labeled A through E) are shown on the overall view. The individual fluid inclusions are shown at higher magnification in the surrounding photographs. These inclusions have a variety of liquid-gas ratios, and two (A and B) also contain solids (crystals). From this sample, we obtained data that we believe, on the basis of our experience with similar materials, are representative of the opal-forming fluids from the Querétaro area.

Microthermometry—Heating. Homogenization temperatures were obtained from two-phase, aqueous liquid-gas, inclusions in one of the four samples mentioned above (not shown). The inclusions homogenized to a single liquid at about 160°C , just as the sample cracked and broke apart (*decrepitated*). Two of the other samples with two-phase, liquid-gas, inclusions decrepitated prior to homogenization.

The fluid inclusions in the fourth sample (figure 5) did not homogenize when heated to 150°C (the maximum temperature to which we heated them in order to avoid fracturing at 160°C), which indicates that they formed at a temperature higher than 150°C , in qualitative agreement with the 160°C homogenization temperature found in the specimen mentioned above. Subsequently, valuable chemical information was also obtained from these fluid inclusions.

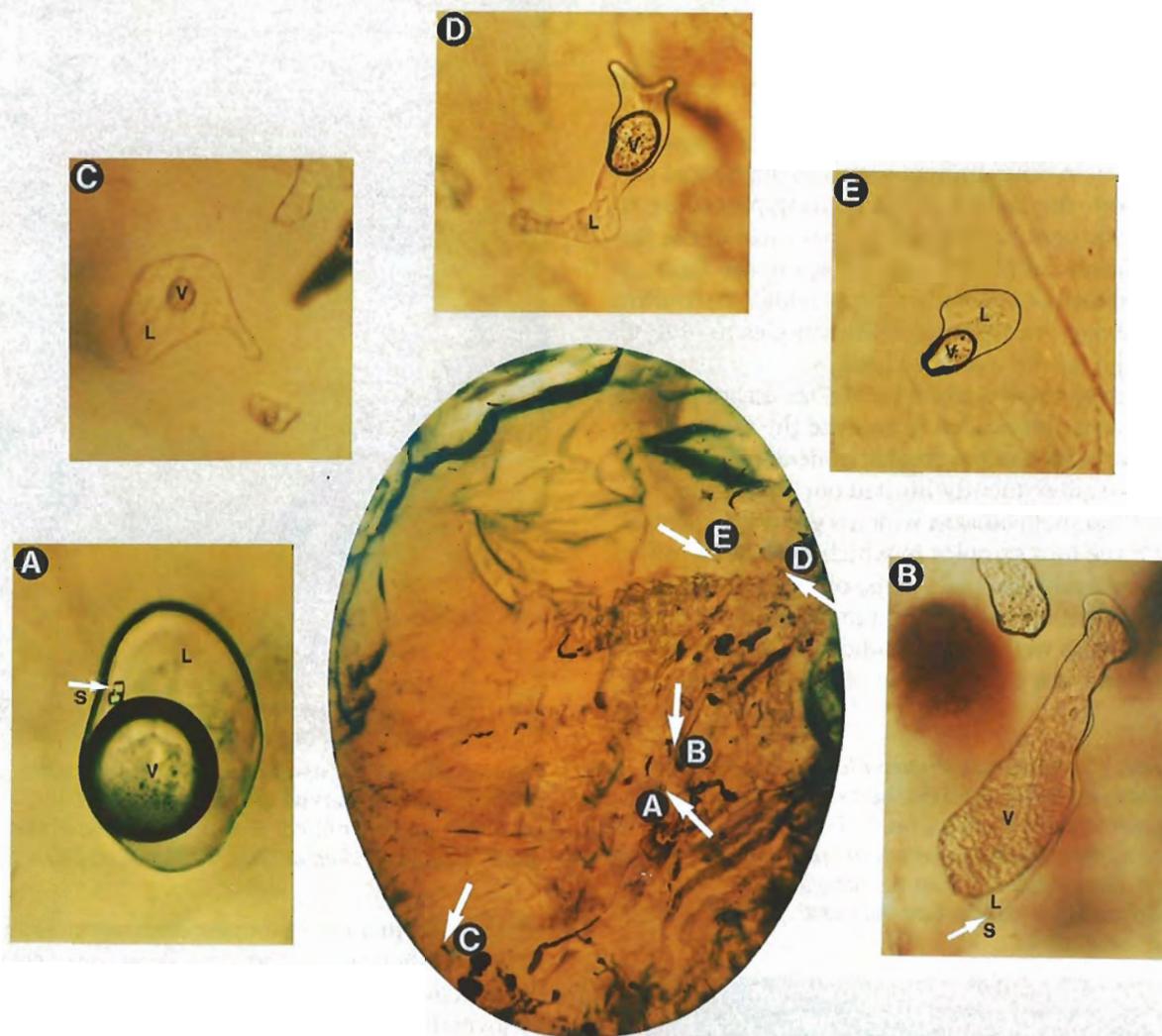


Figure 5. This specimen provided some of the most important data for this study. The large photograph is an overall view of the oval-shaped Querétaro opal, which is approximately 1 cm in longest dimension. Several individual fluid inclusions in the stone are labeled, A through E. Enlarged views of these fluid inclusions show liquid (L), solid (S), and gas (vapor-V) phases, as appropriate. See text for further details. Magnification of the individual inclusions is 235 ×.

Microthermometry—Freezing. Fluid inclusions in the sample shown in figure 5 were frozen (solidified) by circulating nitrogen gas through liquid nitrogen and blowing the resultant cold gas (temperature about -195°C) across the sample. All measurements were made during warming because the inclusion fluids are metastable on cooling; that is, *supercooled liquid* persists to a very low temperature (-100°C) before solids form. The solidified fluids (ice is an example of a solidified fluid) melt with a *reversible or equilibrium* behavior (ice may not form on cooling until -100°C , but if pure it will always melt at 0°C).

Fluid inclusions A and B (figure 5) began to melt when the frozen inclusions were warmed to about -22°C . This is the $\text{H}_2\text{O-NaCl}$ eutectic temperature; that is, it is characteristic of fluids that are domi-

nantly $\text{H}_2\text{O-NaCl}$. The final melting temperatures for these two frozen fluid inclusions were -2.1°C and -7.7°C , respectively, which indicates *salinities* (NaCl content) from near seawater composition (3.5 wt. %; seawater ice melts at -1.9°C) where the melting point is -2.1°C , to salinities about three times seawater where the melting point is -7.7°C .

Frozen fluid inclusions C, D, and E behaved quite differently on warming. They began to melt at about -8°C , that is, at significantly higher temperatures than did frozen fluid inclusions A and B. Frozen fluid inclusion C had a final melting temperature of $+0.6^{\circ}\text{C}$, whereas frozen fluid inclusions D and E both had a final melting temperature of $+1.7^{\circ}\text{C}$. Other frozen fluid inclusions from this sample (not shown) had final melting temperatures as high as $+1.8^{\circ}\text{C}$.

These high final melt temperatures indicate the melting of a *clathrate*, rather than ice. Mass spectrometry was used to identify the composition of this clathrate as well as that of the saline inclusions A and B.

Mass Spectrometry. When fluid inclusion B was cracked, the released gas produced a spectrum in the mass spectrometer that showed only H₂O (figure 6, left; the NaCl present is not detected by the mass spectrometer because it is not gaseous). However, the vapor released when fluid inclusion C was cracked produced a spectrum (figure 6, right) that shows significant carbon dioxide (CO₂ major peak at mass 44) in addition to H₂O. Because other fluid inclusions may have opened at the time the sample was broken, it is difficult to quantify the composition of any individual inclusion.

Mass spectra were also obtained from 29 samples containing one- and two-phase (fluid-solid) inclusions (again, see figure 4). These mass spectra showed only H₂O peaks. We did not observe other gases (such as nitrogen or oxygen) in any of the fluid inclusions analyzed. We believe, because only H₂O was released and because of the heating and freezing behavior of these fluid inclusions, that they contain hydrous silica gel. Although no gaseous phase was produced in the stretching experiments discussed above, the very high vacuum conditions of the mass spectrometer enabled the extraction of H₂O from the hydrous gel.

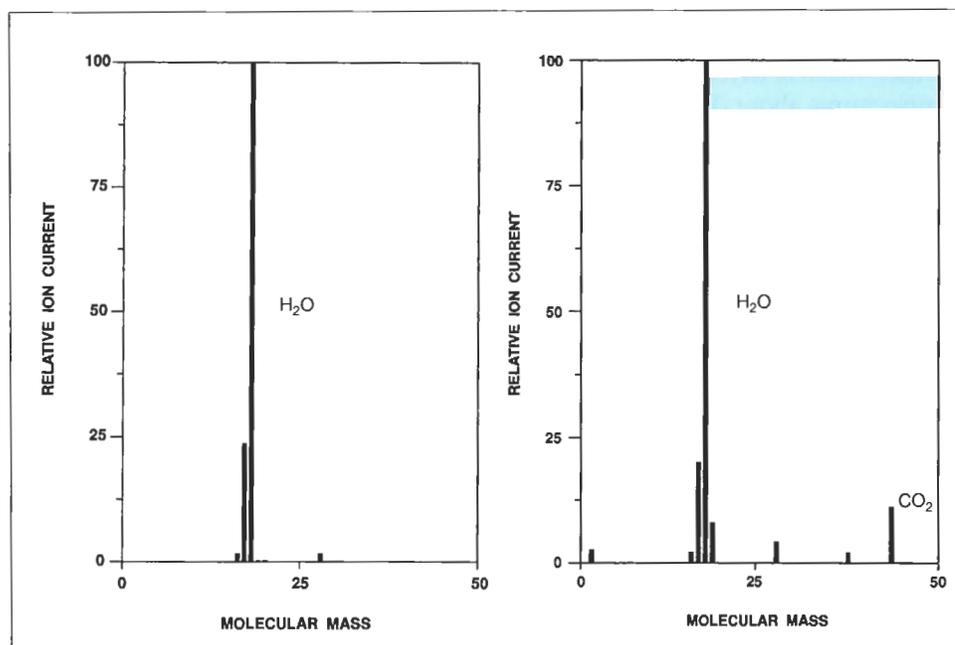
DISCUSSION

Like numerous other researchers (see, e.g., Roedder, 1984), we believe that large, isolated, fluid inclusions similar to those found here are primary and were trapped as the opals formed.

The most common type of fluid inclusions observed in the Mexican opals we examined were one- and two-phase, fluid and fluid-solid. We did not attempt to identify the solid phases, which have been studied in detail by Koivula et al. (1983) and Gübelin (1985). Because these fluid/fluid-solid inclusions (see figure 4) exhibited no change on heating or cooling and produced spectra that showed only water in the mass spectrometer, we interpret these inclusions to be dominantly hydrous silica gel, and we believe that the opals formed from these gels. The solids in the fluid inclusions are likely "trapped" rather than "daughter" crystals, in agreement with the conclusions of earlier workers (Koivula et al., 1983; Gübelin and Koivula, 1986). The "trapped" crystals, labeled "S" in figures 5A and 5B, are rhombohedral and have high birefringence, so they are assumed to be a carbonate mineral (e.g., calcite).

Homogenization temperatures were obtained from fluid inclusions in one sample that contained an aqueous liquid and gas at room temperature. The fluid inclusions homogenized to a liquid at about 160°C, just as the opal decrepitated. The temperatures obtained from these fluid inclusions and the failure of any of the two-phase, liquid-gas, inclusions from oth-

Figure 6. These mass spectra reveal that fluid inclusion B (left) of figure 5 contains only water, and fluid inclusion C (right) of figure 5 contains both water and carbon dioxide (CO₂). Relative ion current is a measure of the abundance of the gases.



er samples to homogenize up to 150°C indicate that these opals trapped fluids during their formation at temperatures near or slightly above 160°C.

NaCl is believed present in inclusions A and B of the stone shown in figure 5 on the basis of their melting temperatures. Carbon dioxide was identified in inclusions C, D, and E of this same specimen on the basis of melting point and mass spectrometry, and we believe that the low-temperature solids observed to melt above 0°C in these fluid inclusions are CO₂-H₂O clathrates.

The wide range of liquid-gas ratios in the fluid inclusions from the sample shown in figure 5 also suggests that both phases are primary. Because these inclusions do not contain atmospheric gases (nitrogen or oxygen), we conclude that the different liquid-gas ratios are not a result of the leakage of fluids and their replacement by a gas. Rather, these inclusions were trapped in a system in which both liquid and gas were present (i.e., a boiling system) in varying proportions and represent the composition of the opal-forming solutions.

SIGNIFICANCE FOR EXPLORATION

The data obtained in this study permit us to speculate both on why gem-quality opals of the Mexican type appear to be unique to this area and on the geologic setting in which additional deposits might be found. It is important to recognize that these gem materials occur in rhyolitic lava flows as secondary fillings in gas cavities or other available sites (Koivula et al., 1983). Rhyolite in general, and rhyolitic flows in particular, are much less common than basalt and andesite, the most abundant types of volcanic rocks. Further, rocks of rhyolitic composition crystallize at temperatures about 300°C lower than those of the more abundant volcanics (rhyolite, 800°C; basalt, 1100°C). The silica (SiO₂) content of rhyolite (70%) is also considerably higher than that of basalt (50%), and the contents of other major elements (Fe, Mg, Ca, Al) are much lower.

The interaction of waters of moderate salinity (whose origins could be either meteoric or hydrothermal, or mixtures of both) with surrounding rhyolitic rocks will result in waters with a high proportion of silica in solution, but low contents of other elements. Such waters probably obtained their high dissolved silica content, the precursor to the hydrous silica gel, through interaction with rhyolites while they were still hot. Subsequently, the opal precipitated from the hydrous silica gel in cavities and other appropriate sites as the water cooled to 160°C. For these opals to have been preserved, it is essential that the host rocks were never reheated above this temperature.

The several required factors—the rhyolitic composition of the rock (particularly the high SiO₂), the low abundance of other elements (e.g., Fe, Mg, Ca, Al) that might have resulted in the precipitation of other minerals (e.g., zeolites, clays), the proper water temperatures for both leaching and precipitation, and the absence of overheating—in combination resulted in the rare occurrence of this gem material. Further exploration must take these factors into account.

CONCLUSIONS

The "fire" opals mined in Querétaro, Mexico, are interpreted to have formed at temperatures near or slightly above 160°C, in a hydrothermal system isolated from the atmosphere, from a hydrous silica gel that is present in many of the fluid inclusions. The aqueous fluids contain mixtures of H₂O, NaCl, and CO₂ that were trapped in some fluid inclusions. It appears that some of the fluids underwent *phase separation* (boiling) during formation of the opals. Because carbon dioxide—along with different proportions of H₂O—is preferentially lost from fluids during phase separation, this resulted in the trapping of different proportions of aqueous liquid, water vapor, carbon dioxide, and sodium chloride.

Exploration for Mexican-type opals elsewhere in the world must consider the unusual combination of geologic factors required to form this type of deposit.

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