Diffusion in gemology can be defined as a method of artificially coloring gemstones, not unlike the dyeing of cloth.

By John L. Emmett, PhD

Diffusion is actually a very common process that we meet in many different contexts. The dying of natural textile fibers is a diffusion process, which is why the longer the fabric is in the dye pot, the darker the color achieved. The color deepens because the dye diffuses deeper into the fiber and makes a thicker and thus darker color layer.

While diffusion processes can be useful in producing low cost gems from very low value rough if it is clearly disclosed at all levels in the marketplace, it is a fact that all the diffusion processes in gemology that are used to color gemstones have been brought to the marketplace without disclosure. One would be naïve not to assume that in all cases the objective was to defraud the buyer.

Chemistry in a Solid
Most people are familiar with chemical reactions in a liquid—for example the reaction between vinegar and baking soda. The two chemicals in this case are brought in contact with each other by mixing—putting a spoon into the mixture and stirring. Two chemicals in a solid can react with each other also. But we can't stick the spoon in to stir them.

So how do two chemicals in a solid get together? They find each other by a process called diffusion.

Chemical reactions take place in solids much as they do in liquids. The difference is simply that we can stir liquids to mix the chemicals, but in a solid it is the diffusion.
Diffusion is a process by which atoms and ions can move through solid matter if the temperature is sufficiently high. So just how does an ion or atom move through a material that is, after all, solid?

Solids are not completely solid. There is some space between the ions (atoms) in the crystal and, even more importantly, there are places in the crystal where ions are completely missing. We call these places where ions are missing, vacancies. Given enough thermal energy (a high enough temperature), a foreign ion can squeeze between existing ions and jump into a vacancy and thus move through a crystal. When it does so, it leaves a vacancy behind. Thus a foreign ion can move through a corundum (ruby or sapphire) crystal by jumping from one vacancy to the next.

Characteristics of Diffusion
Since vacancies are randomly distributed throughout a crystal, the diffusing ion will jump forward or back, up or down, right or left. This staggering path is known in physics as the "random walk" or "drunkard's walk." However, averaged over a large number of jumps, the ion always moves away from regions of high concentrations of the ion, to regions of lower concentration. This principle of always moving away from high concentrations of similar ions towards low concentrations is fundamental to our understanding of the diffusion process. It is just another way of stating that any physical system that is free to move will move to minimize its energy. That is why water always runs down hill, and if we pick up a rock and then let go of it, it will fall to the ground, minimizing its potential energy.

Due to the random walk nature of diffusion, the depth of penetration does not increase linearly with time, but rather it increases with the square root of time. Thus doubling the diffusion depth takes four times as long, and tripling it takes nine times as long, etc. Diffusion coefficients increase very rapidly with increasing temperature (exponentially) as measured from absolute zero, because the number of vacancies increases with temperature and the number of jumps an ion makes per second increases with temperature.

We can speed up the diffusion process by raising the temperature. As we raise the temperature, the number of vacancies increases dramatically and the number of jumps a diffusing ion makes per second also increases. In fact, as we approach the melting point, the number of vacancies and loose ions increase so dramatically that the crystal finally falls apart—that is, it melts.

Mass Transport in a Solid:  
\[ \nabla^2 C = \frac{1}{D} \frac{\partial C}{\partial T} \]

Heat Transport in a Solid:  
\[ \nabla^2 T = \frac{1}{k} \frac{\partial T}{\partial t} \]

\[ C = \text{Concentration} \]
\[ D = \text{Diffusion coefficient} \]
\[ T = \text{Temperature} \]
\[ k = \text{Thermal diffusivity} \]

Heat transport and mass transport in solids are described by the same equations.

No, I don’t expect you to understand these two equations, but what they show is that they are exactly the same! That is, the way that foreign ions on the surface of a crystal diffuse into its interior is exactly the same way that heat applied to the surface of a solid diffuses into its interior. Diffusion of heat or foreign ions into a solid is governed by the same equations.

Baking potatoes is the same diffusion type process as diffusing ions into gemstones and thus follows the same
principles. When these potatoes are baked in an oven, the heat applied to the surface of the potato (by the oven) is diffusing inward, raising the internal temperature and thus “cooking” it. The large potato is about twice as thick through its center as the smaller one. Since diffusing twice the distance requires 4 times the amount of time, the large Idaho potato needs an hour to cook while the French fingerling potato will cook through in 15 minutes. When you think about diffusion processes in gemstones, think about how a potato would cook. If it wouldn’t happen in a potato, it wouldn’t happen in a gemstone either.

The first external diffusion process introduced titanium to sapphires to produce these blue stones. Photo on the right shows the diffused stones in immersion. Photo courtesy of Shane McClure.

The first corundum diffusion process brought to market produced blue stones. Titanium was diffused into the colorless material that results from heat-treating some of the geuda from Sri Lanka. In this case the inward diffusing titanium chemically reacts with the existing iron in the stone forming the Fe-Ti pairs that are responsible for the blue coloration. This diffusion process is carried out at a very high temperature that damages the surface of the gems, so following heat treatment the stones are slightly recut. When the stones are immersed in an index matching liquid the facets appear to be outlined in a darker blue color. Remember this photo as we will discuss this blue facet outlining later.

The photos at top of next column are before (left) and after (right) photos of a diffusion experiment we conducted about 20 years ago. When mine-run geuda from Sri Lanka is heat-treated, much of it turns essentially colorless. The faceted stones on the left are these, but the color has been enhanced a little in Photoshop so you can see that there is some very pale blue or yellow coloration in some of the stones. The stones were packed in alumina powder containing a small percentage of titanium dioxide (TiO₂), and then heated at 1675°C for 150 hours. The stones after diffusion are shown on the right, which is the actual color, not enhanced. Note there is a wide range of depth of coloration that reflects a wide range of the naturally occurring iron concentration in the geuda. Also note the damage to the faceted surfaces; that is why the stones are slightly recut after diffusion.

Types of Diffusion

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<thead>
<tr>
<th>Surface</th>
<th>Bulk or Lattice</th>
<th>Boundary or “Short Circuit”</th>
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Before getting deeper into the phenomenology of diffusion, it is worth noting that there are at least three types: surface, bulk or lattice, and boundary or “short circuit.” Surface diffusion occurs when a small amount of the material to be diffused is placed in a very thin layer on a surface, and then heated. Even though it does not melt and flow, it does move over the surface by diffusion. Bulk or lattice diffusion refers to the process where the diffusing ion moves directly into the bulk of the crystal in quite a uniform manner. Boundary or “short circuit” diffusion occurs when the crystal has a very high density of dislocations or internal structure such as the layering found in micas and the alternating composition layering of the feldspars. Along these layers or boundaries or dislocations, diffusion is very much faster that through the bulk. Examples follow.

This wafer in the photo above was ground from one of the titanium-diffused faceted stones. It is a good example of what is termed bulk diffusion. Note that the diffusion front moves inward quite uniformly. The diffusion depth is about 0.2 mm thick. You can also see the surface damage that is caused by this process and thus why the stones have to be slightly recut.

Copper diffusion into labradorite. Photo by John L. Emmett.

This wafer in the photo above was ground from a labradorite crystal and then diffused with copper at 1100°C. Again, this is mostly bulk diffusion but with some irregularities.

Surface and lattice diffusion in a Sri Lanka sapphire. Photo by John L. Emmett.

This wafer in the photo above was ground from another of the titanium-diffused sapphires. However, in this case it exhibits both surface and bulk diffusion. This gem had a few fingerprint inclusions that reached the surface. The open surfaces of these fin-
gerprint inclusions supported fast surface diffusion of titanium. The surface diffusion rapidly traversed their whole length, and then started diffusing into the bulk from these surfaces also.

Aluminum nails will reduce the cooking time of a potato. Photo by John L. Emmett.

Short circuit diffusion is familiar also. Some years ago the kitchen gadget shops were selling heavy aluminum nails to reduce the time it took to bake a potato. The idea was simple – the heat would diffuse far more rapidly down the aluminum nails than through the potato. Thus the potato could be heated both from within, and from without. Since this cut the diffusion depth of the potato by a factor of 2, it could potentially cut the baking time by a factor of 4. With a few of these nails in each end of a very thick potato, it actually worked.

The photo above shows a stack of plasterboard for the walls of a house. It is a very layered geometry. If left out in the rain with the large flat sides up, it would take a very long time to wet the middle of the stack. However, if oriented with the edges up in the rain the center would become wet much more rapidly. Many minerals have layered structures also and they exhibit short circuit diffusion.
Here is another layered structure from a local Home Depot store. In this case there is a three-dimensional structure, and again short circuit diffusion would occur along all the interfaces. The feldspars, which are primarily mixtures of two end member compositions, have a tendency to unmix as the mineral cools from its formation temperature. This unmixing often forms a layered structure. These layered structures can exhibit beautiful optical effects such as the extremely monochromatic labradorescence of some labradorites, to the subtle adularescence of fine moonstones. When diffused, these layered structures exhibit dramatically anisotropic diffusion rates as a result of short circuit diffusion.

This piece of copper-diffused labradorite shows both bulk and short circuit diffusion. Note that the bulk diffusion has moved about 10% of the transverse dimension, while the short circuit diffusion has completely traversed the slab.

No, this is one of the purple carrots naturally grown in a garden. Am I wasting your time with this illustration? I hope not. As gemologists it is very important to understand that not all sharp color boundaries are caused by diffusion, but such color gradients should raise concern. Not all diffusion occurs in a laboratory, it happens in nature also. Again, not all sharp color boundaries are caused by diffusion. In most cases they are caused by a change in the chemistry of the crystal growth environment.

As mentioned earlier, diffusion depth does not increase directly with time. I want to emphasize that it only increases with the square root of time. This slide illustrates that fact graphically, showing the penetration in 1, 10, and 100 hours into a thick plate. This is simply a drawing, not an actual experiment.

So what happens when a small round pebble is diffused so that diffusion is occurring from all the outside surfaces at the same time? Again, diffusion moves in the direction of the lowest concentration, which is the middle of the stone. If the diffusion is conducted for a long enough period of time, the entire pebble will come up to the same concentration. However, the last place to reach that concentration is the center.

The magnificent steak in our lead photo for this story illustrates a real example of the diffusion discussed above. We know that the color of the meat changes with tempera-

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ture as the heat diffuses in. The color change is clearly apparent in this photo. Notice also that the color boundaries become more and more circular as the diffusion boundary moves farther in. This is a direct result of the fact that diffusion always moves in the direction of minimum concentration, or in this case, minimum temperature.

Do you remember the darker blue facet outlining on the titanium-diffused sapphires shown earlier? How does that come about? Well, imagine cutting off a flat slice of the brown layer from the top and the bottom of this steak. Then imagine cutting straight down the side to remove the brown layer. What is left of the brown steak? Just the brown in the corners remains where the sides meet the top and bottom. This is exactly why after the titanium-diffused stones are slightly recut, the darkest colored blue remains under the facet edges.

A couple of years ago, I listened to a lecture by a gemologist who showed a slide of a piece of the cuprian tourmaline that had a deeper blue color in the center than near the edges. He said that this was a good indication that the piece had been diffused because the coloring ion had diffused in from all sides and would, of course, concentrate in the middle. This will not happen. The fundamental principle of diffusion is that it always moves in the direction of lower, not higher, concentration. When diffusion is inward from all surfaces, the sample can only come to a constant concentration everywhere, and the middle will be the last point to come to that concentration. Remember, water does not run up the side of a mountain.

The next time someone tries to tell you that a diffusing ion will concentrate in the middle of a stone, ask them if they have ever been served a steak that was well done in the center and rare on the outside. What I want you to remember is that if you cannot see how you might achieve a given diffusion effect by cooking a steak or baking a potato, it is probably not a diffusion effect at all.

**Beryllium**

Beryllium diffusion is the latest fraud to be foisted off on the gem community under the guise of a “new mine” or a “new process,” but certainly not as diffusion. This is one of the earliest photos of a beryllium-diffused stone. Note that the color layer is quite thick as compared to what we have seen with the titanium-diffused sapphires. As a matter of fact, diffusion entirely through the smaller stones can be achieved in a few days, since beryllium diffusion in corundum is much faster than that of titanium.

These two pieces of high-purity synthetic sapphire have been diffused with beryllium. Note the orangish-brown coloration as compared with the yellow in the previous photo.

The following photos show the results of beryllium diffusion treatment to a small parcel of Ilakaka, Madagascar sapphires. Note the wide variety of colors produced.
Songea, Tanzania sapphire before and after diffusion treatment. Photo by John L. Emmett.

These Songea, Tanzania sapphires in photo above were beryllium diffused. It is interesting to note that the hues produced are in this case quite similar, but with variations in the degree of saturation.

King's Plain, Australia sapphire before and after diffusion treatment. Photo by John L. Emmett.

Beryllium diffusion of basaltic sapphire from King's Plain, NSW, Australia produces rather dramatic results. Nearly opaque dark blue stones are rendered lighter blue while nearly all of the remainder becomes strong yellow. The yield of cuttable sapphire has been dramatically increased by beryllium diffusion.

The Many Colors Produced by Diffusion
Titanium diffusion produces only blue, yet beryllium diffusion produces many colors. Why?

Corundum is comprised of only aluminum and oxygen (Al₂O₃). Neither of these ions absorb light in the visible region of the spectrum, which is why pure corundum is colorless. When titanium is diffused into iron-containing sapphire, only a blue color is formed. That is because the only reaction with titanium that produces color is with iron (forming the Fe-Ti pairs). The situation is quite different with beryllium diffusion.

In corundum the aluminum is present as Al³⁺ and the oxygen as O²⁻. If we now diffuse in beryllium it will locate on aluminum sites, not oxygen sites. But there is a problem. Beryllium ions are Be²⁺ not ³⁺ like aluminum so something has to give as the crystal must remain electrically neutral. What happens is that one of the nearby oxygen ions that is O²⁻ becomes O¹⁻. This strange type of oxygen ion is referred to by physicists as a “trapped hole.” This so called “trapped hole” can easily move from one oxygen ion to another throughout the crystal. While O²⁻ does not absorb visible light, the trapped hole, O¹⁻, does, and creates the colors we have seen in the previous slides.

The way that the trapped hole absorbs light, and thus the apparent color we see, depends to some degree on what type of metal ion is close to it. If it is close to beryllium, the color is the orangish-brown. If close to iron, it is a golden-yellow, and if close to chromium, it is orange. It is interesting to note that the trapped hole has a preference for which metal ion with which it chooses to associate, if several are present in the crystal. Its first choice among the common trace elements in corundum is chromium, followed by iron and then by beryllium or magnesium. Beryllium diffusion can also lighten very dark blue sapphires by the trapped hole oxidizing the iron in the blue-forming iron-titanium pairs, but that is another whole lecture.

How fast is diffusion?
To achieve 80% diffusion saturation of a 6mm diameter corundum pebble at 1800°C, would require the following:

<table>
<thead>
<tr>
<th>Diffusing Ion</th>
<th>Required Time</th>
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<tbody>
<tr>
<td>Iron or Chromium</td>
<td>30,000 years</td>
</tr>
<tr>
<td>Magnesium</td>
<td>5 years</td>
</tr>
<tr>
<td>Titanium</td>
<td>5 months</td>
</tr>
<tr>
<td>Beryllium</td>
<td>1.2 days</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>15 minutes</td>
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Diffusion rates are strongly dependent on temperature, but also they depend very strongly on the type of ion being diffused. The chart above compares a selection of ions that range from the slowest to the fastest. Generally, the slowest ions are those metal ions with the same charge as aluminum, i.e. ³⁺ like iron and chromium. Metal ions with a different charge than aluminum, such as those with a charge of ⁴⁺ like titanium, silicon, and zirconium, dif-
fuse much faster, as do those ions with a charge of 2+ like magnesium and beryllium. Hydrogen with a charge of 1+, and effectively zero size, is the fastest of all.

**What Temperature is Required for Diffusion?**
When the conjecture arose that some of the red andesine or labradorite might be colored by copper diffusion, some pundits commented that plagioclase could never be heated to the temperature used to diffuse corundum, and thus it could not be copper diffused. That illustrates a common misconception about diffusion in solids.

What is necessary for diffusion in an arbitrary crystal to occur in a realistic timeframe, is that the crystal be held at a temperature that is 85-90% of its melting point (as measured from absolute zero), not the melting point of corundum. Compare corundum, labradorite, and ice. All three can be successfully diffused, and at dramatically different temperatures: corundum at 1800°C (melting point is 2050°C), labradorite at 1150°C (melting point is 1300°C), and ice at -27°C (melting point is 0°C). Just a note of explanation – absolute zero is 0 Kelvin, or -273° Celsius, or -459° Fahrenheit.

**Which Gemstones Can Be Diffused?**
To be a candidate for diffusion, a gemstone must be able to be heated to about 90% of its melting point or solidus point (as measured from absolute zero) without decomposition. Stones containing significant hydroxyl (OH) or fluorine usually decompose. Two examples:

**Topaz** – decomposes into mullite, water, and SiF₄ well below an estimated melting point.

**Chrysoberyl** – Melts without decomposition at 1870°C.

So, can all gemstones be diffused? No, but some can. Topaz can’t, it decomposes into mullite, water, and silicon tetrafluoride at a very low temperature, while chrysoberyl probably can, as it holds together right up to its melting point.

Diffusion is not always from the outside in. When gemstones are heated for any reason, inclusions in them may start to diffuse in to the bulk of the crystal. The drawing at bottom left is of individual blocky rutile crystals diffusing into the main corundum crystal during normal heat treatment.

This photo above is an actual example from one of our experiments, showing exactly that diffusion process in action. It also shows another interesting process at work. The smallest of these rutile inclusions just diffuse into the corundum as described on the previous slide. However, if large enough, the larger ones can fracture the corundum because they expand much more than the corundum does when they are heated to high temperatures. Then surface diffusion spreads the titanium over the surface of these fractures, and from there into the corundum crystal by bulk diffusion. Since these fractures usually don’t reach the surface, they completely close when cooled, eliminating the reflection from the interface. Thus they remain as non-reflective blue discs when cool. Interestingly, they are parallel to the basal plane of the crystal.
illumination, while the right is in darkfield illumination. The wafer is cut and polished so that the c-axis is perpendicular to this page. In the “before” photo, the brown material in the brightfield photo arrayed in the hexagonal pattern is primarily microscopic needles of rutile (TiO₂). In the darkfield photo, the rutile stands out with very high contrast as its index of refraction is very high compared to that of corundum and thus it scatters light efficiently. When this wafer was heat treated, the rutile dissolved into the sapphire by the process of diffusion, and reacted with the iron in the stone forming Fe-Ti pairs and thus the blue color. This is exactly the same process as shown in the photo at top of page 6. Note that the darkfield picture after heat treatment shows little light scatter where the rutile was, as it is now in solution.

Why isn’t the hexagonal pattern completely blurred out by diffusion spreading of the titanium? The diffusion time was 150 hours and the titanium moved about 0.2 mm. The wafers at the bottom of page 10 however, were only heat treated for 5 hours, and thus the titanium could only move about 18% as far, but there is also another factor and that is the temperature. The temperature for this heat treatment was 150°C lower than the sapphire at top of page 6, so the diffusion coefficient was much lower also.

The difference between external diffusion, and internal diffusion during heat treatment, is quite simple. With external diffusion we choose what “dye” will be used to achieve our color objective, while with internal diffusion during heat treatment, it is mother nature who chooses the colors.

Going Forward
The latter half of the 20th century saw great innovation in the processing of low quality gem materials to enhance their beauty, and the development continues apace. While such developments could have been brought to market ethically and could have been a great contribution to lower cost jewelry, this was not done. Instead these technological advances were marketed in a way to maximally defraud the customer to the advantage of the seller. Will the gemstone industry always be one that uses its technological innovation for fraud?

About the author: Dr. John Emmett is one of the world’s foremost authorities on the heat treatment, physics, and chemistry of corundum. He is a former associate director of Lawrence Livermore National Laboratory and a co-founder of Crystal Chemistry, which is involved with heat treatment of gemstones.

Editor’s Note:
This article was inspired by the author’s presentation to the delegates attending the World of Gems Conference II. At the request of the publisher he has agreed to structure it using an informal conversational writing style, as opposed to the formal style required of the scientific journals to which he is more accustomed.

Information Regarding this GemGuide Sample Pack

The article presented here is a sample of one of our feature articles that appears in each issue. The Gem Market News portion of the GemGuide book also contains gemological articles, diamond and colored gemstone trends, gem notes, appraiser information, and more. Nowhere in our industry is this quality of information available.

The diamond page that follows is a representative page from the GemGuide. Prices are updated monthly online for your convenience and bimonthly in the printed book. We cover many shapes and also more difficult to find information such as fancy color diamonds, old European cuts, baguettes, triangles, and more.

The colored stone page enclosed is also representative of the more than 70 gem varieties that appear in the GemGuide. More extensive price grids appear for ruby, emerald and sapphire. In addition, separate sections contain pricing for most pearl varieties and opals.

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