

CHAPTER 7

CALCITE: INTRODUCTION TO OPTICAL CRYSTALLOGRAPHY

7.0 Introduction

in 1665 Erasmus Bartholinus discovered that if he looked at a black dot through a calcite crystal two dots appeared. Snail had just forty years before proposed his Law of Signs. Erasmus, in the tradition of "nay-sayers" used his calcite crystal to show that Snell's Law was wrong. In calcite only one ray obeyed Snell's Law, the other did not. Snell's Law not only failed to provide the angle for the strange and extraordinary ray but it provided no explanation of why such a ray should exist at all.

Erasmus was ignored but his discovery was an unavoidable curiosity. Christian Huygens proposed his wave theory for light in 1690 and Newton his particle theory in 1704. Neither theory explained the observations seen by Erasmus though Huygens' model did show how such a ray path could arise. It was over one hundred years before more data was added to the list of calcite's properties and the riddle began to be solved.

In 1808 Louis Malus discovered the polarization of light reflected from water and glass. A seemingly unrelated discovery but when polarized light was used to look at calcite an amazing thing happened. The dots could be made to disappear or reappear, one at a time, by rotating the crystal. Erasmus' discovery and that of Malus began unlocking doors. By 1829 most of the properties of transparent materials that can be characterized using polarized light had been included in an English textbook on Natural Philosophy.

Calcite, the key to characterizing the matter/polarized light interaction, became the source of polarized light in microscopes in the 1830's. In 1828 William Nicol, using Snell's Law of Sines, sliced and then glued the two reoriented pieces of calcite together so that only one ray exited through the crystal along its original direction. Henry Fox Talbot used these "Nicol" prisms in his microscope after first experimenting with tourmaline plate polarizers in 1834. This "Nicol" technique, or a variation of it (Glan's, Thompson's, and Ahren's prisms) is still used today for the most critical applications of polarized light.

In World War II calcite became one of the Ally's secret weapons. The calcite gun sight and bombsight was developed for precision targeting.

The major source of optical calcite was Iceland, hence the name Iceland Spar. The mines in Iceland flooded in the 1950's and have not been reopened. Today most good quality calcite comes from Mexico.

7.1 Optical Properties of Calcite

Erasmus Bartholinus first described the appearance of two images from one when looking through a calcite cleavage rhombohedron. This experiment can be duplicated by putting a black spot on a sheet of paper and placing a calcite rhombohedron over it. Two black dots will appear. If the crystal is rotated one of the dot images stays fixed and one moves. The stationary image obeys Snell's law and passes straight through the crystal. All of these properties are listed below.

1. One dot becomes two images when viewed through a calcite rhombohedron (see Figure 7.1).
2. The distance between the images is proportional to the thickness of the crystal (see Figure 7.1).
3. When the crystal is rotated one dot image remains stationary (see Figure 7.2).
4. The stationary dot image is made by a ray that obeys Snell's law (see Figure 7.2).
5. The dot image that moves does so in a circular motion (see Figure 7.2).
6. The stationary and the moving dot images stay fixed with a linear motion of the crystal (see Figure 7.2).
7. One dot image appears to be higher in the crystal than the other image. This can be seen by moving the head from side to side and noticing that one of the dot images moves in the opposite direction (see Figure 7.3).
8. The higher image is the result of a higher real refractive index along that path (see Figure 7.3).

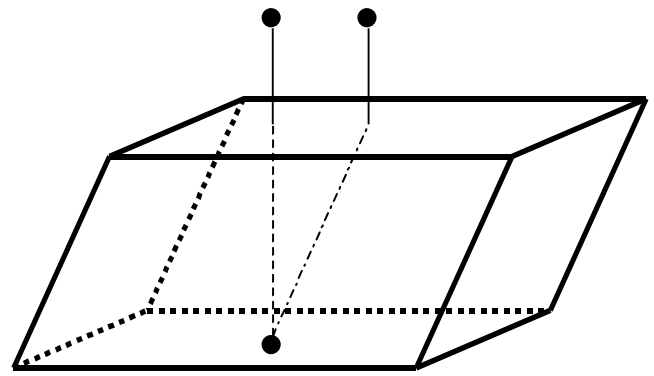


Figure 7.1: The Light Paths Through Calcite

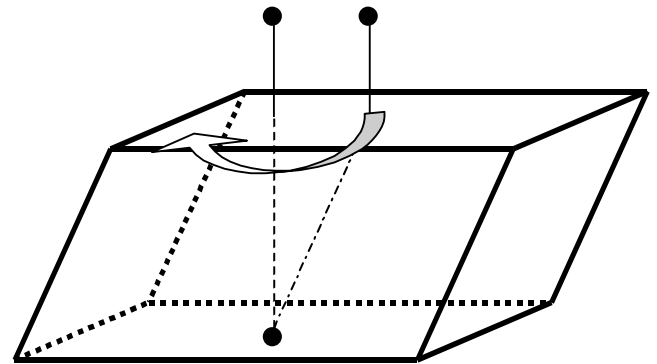


Figure 7.2: Identification of the Stationary and Rotating Image

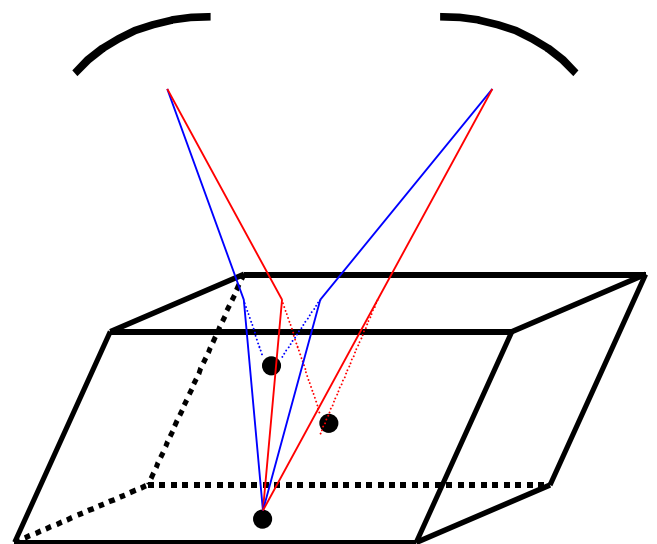


Figure 7.3: Images at Different Depths Due to Refraction

9. There are two distinct refractive indices shown by the crystal (see Figure 7.3).
10. The higher image is the stationary, ordinary image (see Figure 7.3).
11. The refractive index along this path is denoted " ω " (the Greek letter omega) (see Figure 7.3, blue lines).
12. The extraordinary ray refractive index is denoted " ϵ " (the Greek letter epsilon).
13. Crystals are grouped by their optical sign. When the refractive index is greater than the refractive index the crystal is said to have a negative optical sign. Calcite is an optically negative crystal.
14. One of the images is less distinct than the other. This indicates that the light that travels along this path is absorbed more than that along the other path (see Figure 7.4).
15. This less distinct image is the stationary image of the ordinary ray (see Figure 7.4).
16. The ordinary ray has the higher absorption coefficient or imaginary refractive index.
17. The line connecting the two images, a-a, is parallel to the line that bisects the obtuse angle, b-b (see Figure 7.5).
18. There are two corners of the calcite rhombohedron that have three obtuse angles forming a single solid angle.
19. If the crystal is rolled onto another face the same observations are made.
20. The optical properties are symmetric about the line that bisects the solid angle composed of the three obtuse angles. This line projects onto the image of the dots.
21. The image formed by the ordinary ray is nearest the top solid angle composed of the three obtuse angles (see Figure 7.5).

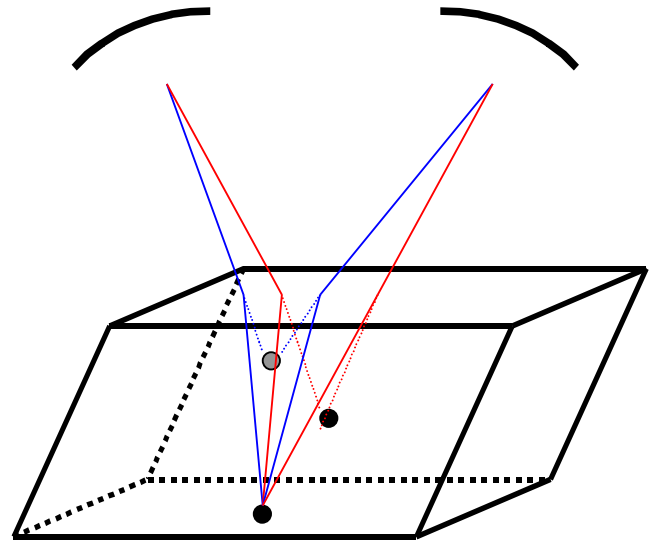


Figure 7.4: Effect of the Imaginary Refractive Index

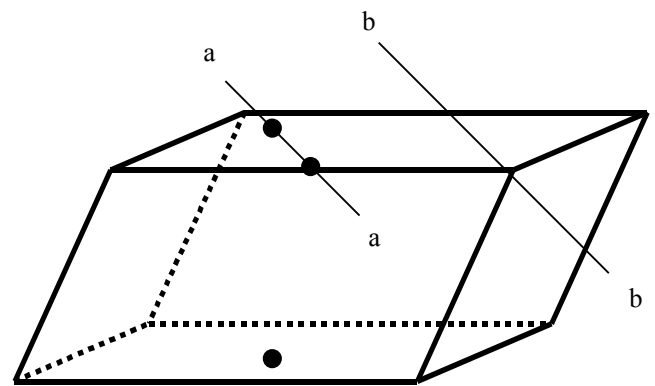


Figure 7.5: Crystallographic Orientation of Images

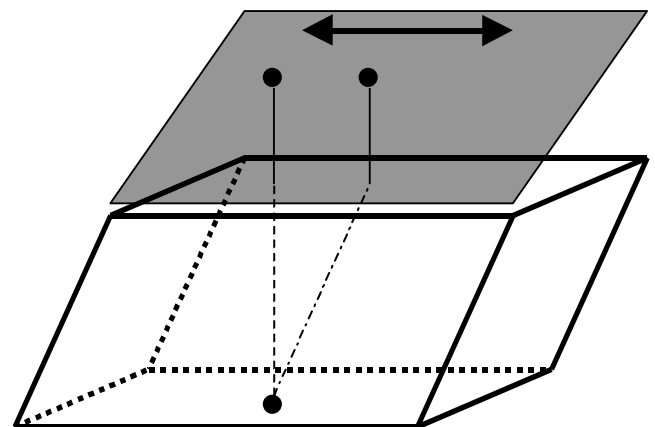
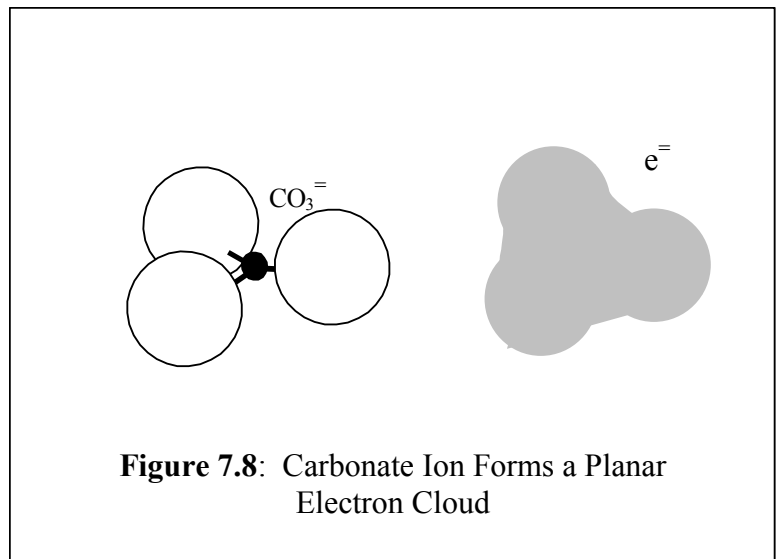
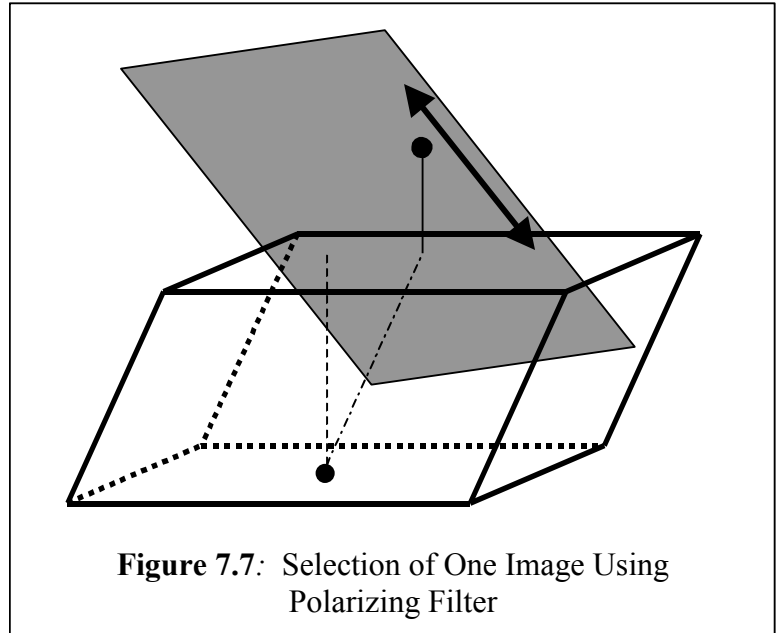


Figure 7.6: Image with Linear Polarizing Filter Parallel to Edge

22. When a single linear polarizing filter is used and the orientation of polarization is parallel to the long edge of the crystal then both images are visible (see Figure 7.6).
23. If the direction of polarization is parallel to the line bisecting the obtuse angles then only one dot image is visible (see Figure 7.7).
24. This dot image is the one formed by the extraordinary ray (see Figure 7.7).
25. If the polarizer is rotated by 90° the other dot image is visible by itself.
26. This is the image formed by the ordinary ray.
27. Each image is linearly polarized as indicated by the fact that one of the images can be completely eliminated by one linear polarizer (see Figure 7.7).
28. Calcite is composed of molecules with the following formula: CaCO_3 .
29. The carbonate ion is a planar structure with a carbon ion at the center of three oxygen ions. It is a very electron dense ion (see Figure 7.8).
30. The relationship between the local concentration of electrons and refractive index indicates that the ordinary ray vibration direction must be in the plane of the carbonate ion.
31. The symmetry of the optical properties indicates that the bisector of the solid angle composed of the three obtuse angles must be normal to the carbonate plane (see Figure 7.9).



32. All of the electrical field energy passing through the crystal when only one image is seen is polarized in one direction and experiences only one electron density.
33. When only one image is visible only one refractive index is shown by the crystal.
34. When the linear polarizer is at 45° to a position where only one image is visible, both images are seen with about equal energy (this point is actually a little closer to the single image position formed by the ordinary ray due to its higher imaginary refractive index).
35. If a second polarizer is used additional properties are evident. When two images are seen with a single polarizer they are still visible when the crystal is between the two polarizers and the polarization direction of the polarizers is at 90° with respect to one another (crossed polars) (see Figure 7.10).
36. The linear polarized beam is changed by passing through the crystal and light traveling along each of the linear polarized paths in the crystal contribute to this change, otherwise only one or no dot image would be visible.
37. When only one image is visible with a single polarizer then the second is added as above the crystal is dark and no image is seen.
38. This dark position is called the extinction position.
39. Calcite is said to show symmetric extinction because it becomes dark between crossed polars when the direction of polarization bisects a characteristic angle of the crystal (the obtuse angle). This is further explained in chapter 8.
40. If a crystal is in its extinction position and one of the linear polarization filters is removed the crystal exhibits only one of its refractive indices.
41. When the crystal is between crossed polars it is brightest when it is rotated 45° from its extinction position.

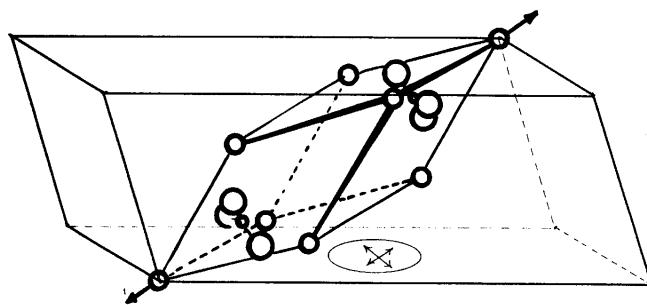


Figure 7.9: Orientation of the Carbonate Ion in the Crystal

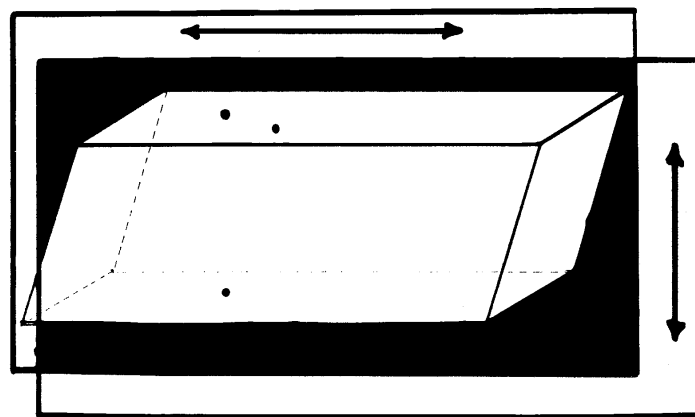


Figure 7.10: Two Images can be seen When the Crystal is Bright between Crossed Polarizing Filters

These observations and conventions have allowed us to determine the orientation of the carbonate ions with respect to the morphology of the calcite cleavage rhombohedron. It has not allowed us to predict the displacement of the extraordinary ray. To predict this effect we need to use the technique developed by Huygens.

Light can be modeled using a line of points that is normal to the propagation direction of the beam. Each point is used as a source for a wave and a curved line is drawn representing the crest of the wave after traveling one wavelength from each source. A tangent is drawn to these curves that connects all of the curves from the different source points. Each contact point between the tangent and the waves is used as the source points for the next wave. As long as the wave velocity is the same in all directions the path of the resultant series of waves is a line parallel to the original direction of the beam. This is the case with the ordinary ray in calcite (see Figure 7.11).

If the wave velocity is not the same in all directions the result is an elliptical wave front from each source. The same procedure use above is applied. The new source points no longer lay on the beam parallel path that the original points were on. A new path is diagramed that is consistent with the path of the extraordinary ray. We can see how this works if we consider another model.

We need a straw and a razor blade to model the wave velocity in calcite along the two preferred directions in the crystal. In this model the carbonate ions are arranged normal to the long axis of the straw. The diameter of the straw represents the wave velocity for the ordinary ray refractive index. If we look straight down the straw we see only one velocity (the diameter of the straw). If we cut the straw at some random angle the result is an elliptical cross-section. The minor axis of the ellipse is the diameter of the straw, The major axis represents the velocity in the extraordinary ray. The velocity in the extraordinary ray varies depending on the angle at which the straw is cut. The major axis of the ellipse is always at right angles to the minor axis of the ellipse (the ordinary ray direction). This is exactly what we saw with the calcite crystal, the ordinary and extraordinary rays are always linearly polarized at 90° to one another. When we plot all possible velocities for the extraordinary ray the result is an ellipse with the major axis corresponding to the wave velocity along the most extraordinary path in the crystal and the minor axis equal to the wave velocity along the ordinary path. If we draw the same plot for the ordinary ray the result is a circle.

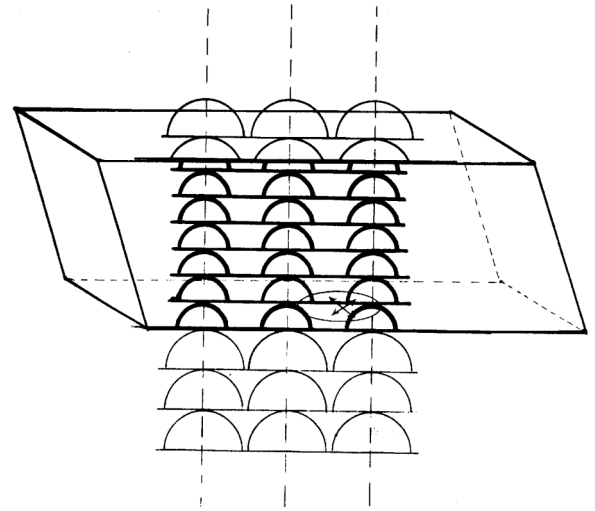


Figure 7.11: Huygens' Construction for the Ordinary Beam

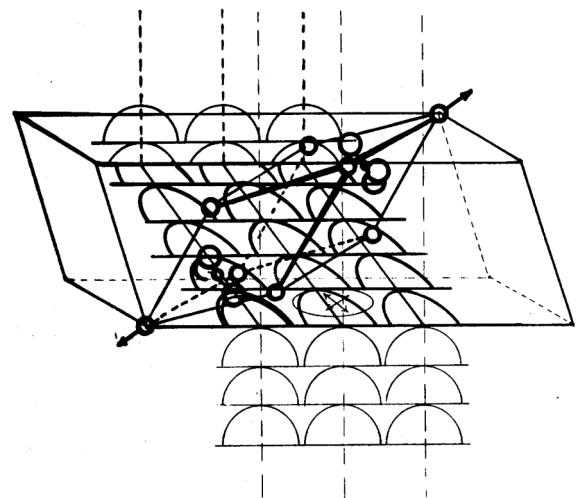


Figure 7.12: Huygens' Construction for the Extraordinary Beam Relative to the Carbonate Ion

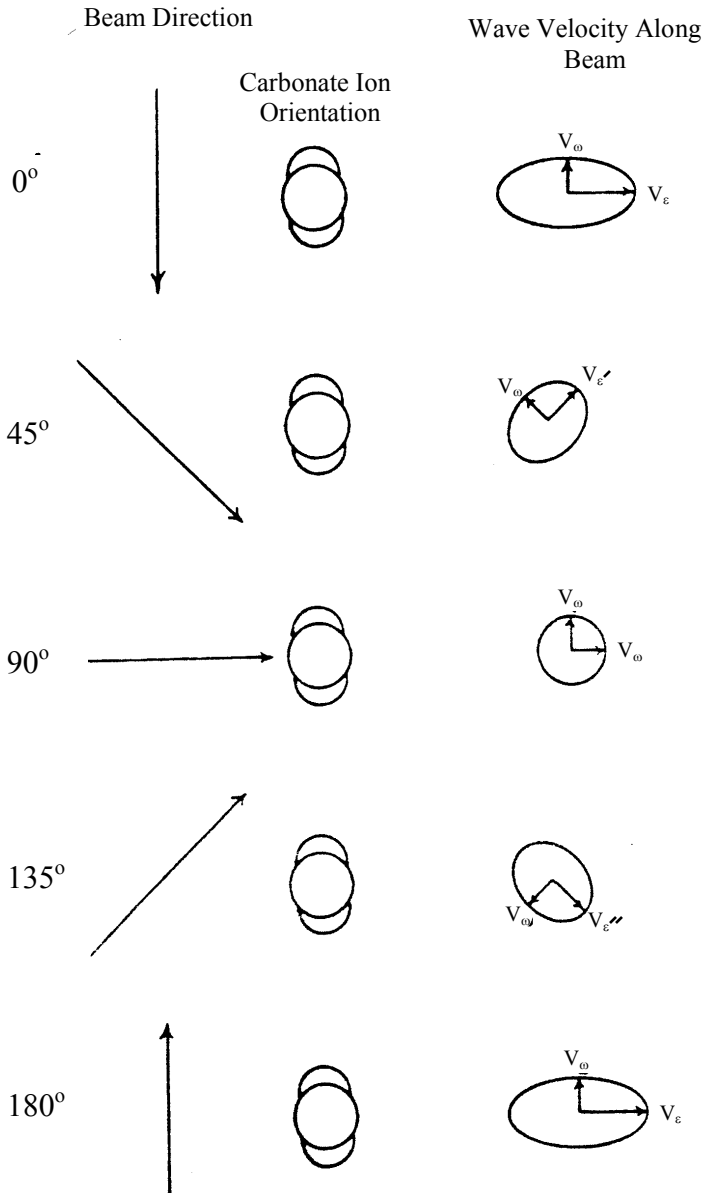
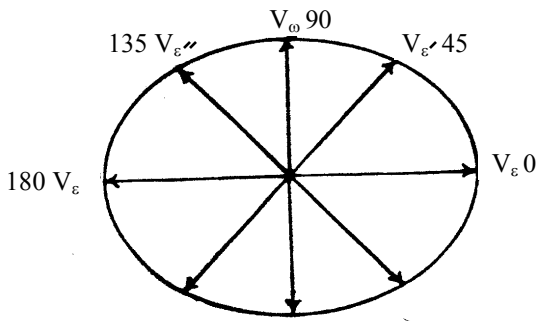
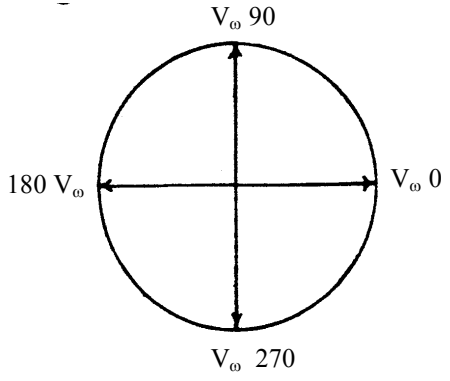


Figure 7.13: Wave Velocities and Directions Imposed by the Carbonate Ion

The wave velocity along each of the preferred vibration directions varies with the direction of the beam through the carbonate ion plane. V_{ω} is the velocity in the plane of the carbonate ion and V_{ϵ} is the velocity normal to the beam direction and the vibration direction of V_{ω} . As a result V_{ϵ} changes value with a change in the beam direction. The Wave velocity drawings (left show the velocity, by magnitude, and direction of vibration for beams of different directions through the carbonate ion. These drawings are from the perspective of looking down the beam. When each of these velocity vectors for all possible directions is collected in one graph the result is shown below. These velocities with respect to beam direction must be used in order to use Huygens' construction for the extraordinary ray direction.

V_{ω} All Have the Same Magnitude

V_{ϵ} Magnitude is Orientation Dependent



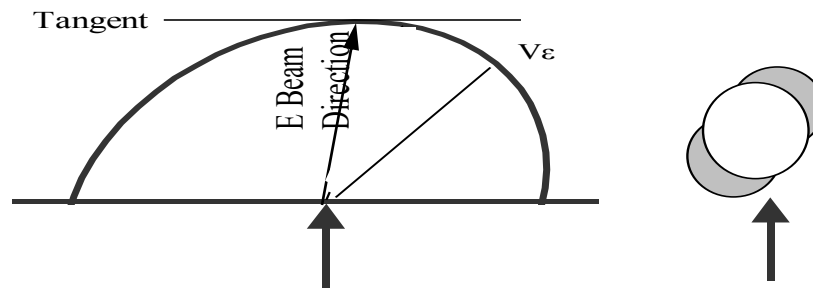


Figure 7.14: Detail of Huygens' Construction and the Calcite Carbonate Ion

Huygens' construction starts with a wave front modeled by a line of spherical waves, all of which are in phase (see Figures 7.11 and 7.12). This series of waves is continued by drawing a line tangent to the wave front of all of these waves and using the contact point between the wave and the tangent as the point from which a new wave begins. In the case of calcite two new waves result from the beam when it enters a crystal. One of these wave fronts continues with a circular wave front but because of the higher electron density has a shorter wavelength. This is the ray whose velocity with orientation is the same in all directions. The other ray, the ray, does not have the same velocity in all directions. The result is an Elliptical wave front. When a tangent is drawn connecting all of these elliptical wave fronts the contact points indicate a change in direction for the beam, This change in direction is not coincident with the major axis of the ellipse but is in fact the orientation taken by the extraordinary ray. This construction is shown in Figures 7.11 and 7.12.

7.2 CONCLUSION

Understanding the interesting optical properties of calcite drove our understanding of light/matter interaction for nearly 150 years. As we will see in the next chapter Rene Haüy unlocked one of the major keys to understanding crystal structure by studying calcite just about 25 years before the discovery of polarized light. John Dalton's development of the atomic theory in 1808 led to a detailed understanding of the chemical composition of calcite. Without this unique mineral our understanding of crystals, chemistry, and optics may have been retarded by centuries. Without Icelandic calcite the Allies may have lost to Hitler, but that is another story (see Elizabeth A. Wood, CRYSTALS AND LIGHT, Dover Press, p. 99, 1977, for more information on the calcite ring site, an Allied secret weapon.)