

Acceptance of the Dana Medal of the Mineralogical Society of America for 2001

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THE BEGINNING

Science has been a passion in my life since my grade school days. My interests in mineralogy began with an interest in the color of small pieces of minerals given to me by a friend. The minerals included fluorite, spodumene and elbaite (tourmaline). I was particularly interested in the color of watermelon tourmaline. Questions to my teachers about the origin of the colors did not yield satisfactory answers. Furthermore, I grew up on the glacial till and was also fascinated that, unlike anything I found locally, a mineral like tourmaline could be transparent like a piece of glass. This curiosity led to a life-long quest to understand color in minerals.

Early on, I realized that chemical analysis was a necessary component of my quest to understand minerals. Initially, this realization was expressed as a series of science fair projects (Fig. 1) that involved minerals, chemistry for their analysis and electronics to build instruments to test their properties. Although I focused on microanalysis (wet chemical tests under a microscope) I was fortunate to have parents who tolerated more than a hundred kilograms of chemicals in the basement and drawers of rocks and minerals throughout the house. At the University of Wisconsin, Eau Claire, I majored in chemistry and math and was given extensive opportunity to explore in the labs. Summer research experiences in Minnesota and Oregon inevitably drifted toward problems of mineral analysis and geological field trips. I had an equally fascinating time as a chemistry graduate student at Caltech studying molybdenum cyanides and oxy- and hydroxy-polymers of iron. After I graduated with a Ph.D., the Division of Geological & Planetary Sciences at Caltech made a bold move to hire a mineralogist who never had a course or any other formal training in his life in the fields of mineralogy, geology, or planetary sciences. The department chairman, Gene Shoemaker, was an effective recruiter, but he didn't have to try very hard. It sounded like a fascinating opportunity. I still am occasionally amazed to wake up in the morning and realize that I am paid to work on something I so fully enjoy.

THE PAST

My early interest in tourmaline evolved into the professional study of mineral spectroscopy, a necessary tool to address the questions that interested me for so long. Tourmaline is a good example to consider. It contains metal ions that can have different oxidation states and that can reside in more than one site. The tools of spectroscopy proved to be highly valuable probes to establish oxidation states and site occupancies of several common cations in minerals. We focused on not only where the bands were but also on the intensities of the bands. We tried to bring quantitative rigor to the application of optical



FIGURE 1. George Rossman (early 1960s) at a Wisconsin Junior Academy of Science competition.

spectroscopy to mineralogy. Quantitative determinations of cations in pyroxenes and amphiboles soon followed, as well as studies into the optical ramifications of interactions between and among cations in adjacent sites. Intervalence charge transfer interactions proved more challenging to study, but were found in most important mineral systems.

The spectroscopic probes also proved well adapted to examining materials that responded poorly to X-ray diffraction such as radiation-damaged minerals, weathering products, and fine-grained minerals such as are found in biominerals.

Inevitably, we noticed that the spectra of minerals also contained absorptions bands from hydroxide ions. Particularly important was the common observation of OH bands in “anhydrous” minerals. These observations led to our systematic investigation of the role of OH in the anhydrous minerals. The timing was fortunate. Other groups were realizing that H₂O played an important role in rheologic properties of minerals, and the industrial community understood the importance of H₂O towards dielectric and optical transmission in synthetic minerals.

We now know that minor to trace amounts of OH and H₂O are common in the nominally anhydrous minerals. They constitute a significant portion of the global hydrogen reservoir. They influence or even control several of the physical and chemical properties of the host phase. Classically, the hydrogarnet substitution (SiO₄ = H₂O₄) was the accepted mode of entry. This substitution was proven in the grossular–katoite series, and was assumed by many to be the way that hydrogen entered silicate minerals. While this model was appealing, the complexity of IR spectra in the OH region indicated that multiple sites are involved in hydrogen incorporation in many of the nominally anhydrous minerals.

There are many reasons to care about hydrous components in minerals and materials. Minor hydrous components have disproportionately large control on properties such as rheology, diffusion, exsolution, and radiation stability. They are part of the overall stoichiometry of the host mineral and play a role in charge compensation of other minor components. They act as geochemical probes of the growth environment, and respond to geologic processes to which the host phase has been subjected. Their role in the melting properties of rocks and their role in the chemical reactions at mineral surfaces are items worthy of much further study.

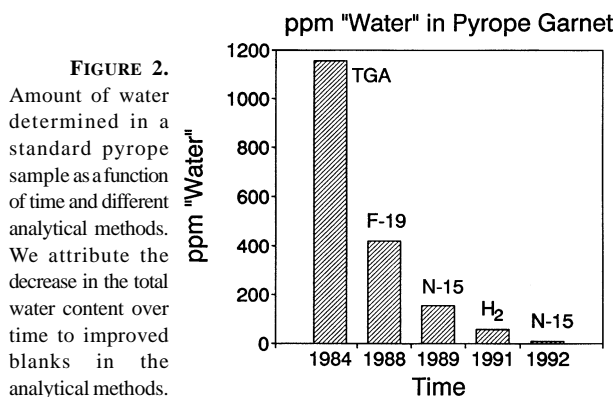
Although historically, it was mechanical strength of quartz that first drew attention to the role of minor hydrous components, we now recognize that the properties of many technological materials are also influenced by their presence. Examples range from the near-infrared transmission of fiber optics, the dielectric properties of ceramic substrates, optical properties of laser crystals, to image and grating storage in fibers and synthetic perovskites.

Traces of OH are found in most silicate minerals. Common examples include quartz, olivines, orthopyroxenes, clinopyroxenes, garnets, plagioclase feldspars, and several oxides. Minerals that incorporate H₂O tend to have open volumes in their structure large enough to accommodate the H₂O molecules. Common examples include the framework silicates such as alkali feldspars, feldspathoids, and ring silicates such as beryl and cordierite.

In all studies of hydrous components in minerals, calibration issues remain difficult. Although infrared spectroscopy is a sensitive way to detect the OH stretch, it is not intrinsically self-calibrating. Several attempts have been made to generate a 'universal' infrared calibration based on glasses and solutions or on individual minerals standards. While these general calibrations do give a reasonable estimate of the amount of H₂O in a crystal, they are subject to sizable error, particularly for minerals with weak hydrogen bonding. Unfortunately, minerals with weak hydrogen bonding include many of the minerals in which the majority of researchers are now interested.

For the purposes of mineral-specific calibrations we have used, over time, a variety of methods ranging from thermogravimetric weight loss, P₂O₅ coulometry, NMR spectra, hydrogen manometry, and nuclear reaction analysis involving ¹⁹F and ¹⁵N nuclear reactions with H. As is usually the case with most developing methods of trace analysis, we have had difficulties with the background. The history of our analyses of a "standard" pyrope over time is illustrative. As Figure 2 shows, the amount of H in our standard sample keeps decreasing with time as we improve our backgrounds. For a while, extrapolation of the steady evolution of the results to ever decreasing values may have indicated to some that the entire field of my studies for the past two decades was soon to disappear in totality as the true hydrogen contents asymptotically decreased to zero. Fortunately this did not happen as, through the efforts of our collaborators, improved ¹⁵N Nuclear Profile Analyses stabilized and converged to agreement with careful hydrogen manometry.

Typical OH concentrations range from a few parts per million (as H₂O) in some olivines and garnets, to hundreds of parts per million in pyroxenes, to 0.1% levels in feldspars. We soon



noticed that mantle phases often had higher concentrations of OH than their crustal equivalents. This observation led to a systematic study of mantle minerals. The results of these studies led us to extrapolate the amount of OH we actually found in isolated mantle samples to a global upper crustal model that concluded that there is the possibility that the integrated OH in just the anhydrous minerals could constitute a volume of water nearly equal to water in all the oceans of the world today. Now, much speculation abounds about the role of hydrous components in deep earth phases, and the role of such minerals in the global hydrogen cycle.

THE FUTURE

As I look to the future, I foresee many areas where scientists trained in mineralogy will have important contributions to make. The growing field of planetary mineralogy will likely address not only phases common on earth, but also other phases attuned to the low temperature regime of the outer planets and their moons. There is a growing integration of mineralogy with computational science that will offer many opportunities in the future. Traditionally, we have focused on bulk solids, but many advances are still to come in the field of mineral surfaces. A related area is the world of fine-grained materials where the surface to volume ratio is large. In this category we will also find many bio-minerals as we explore the interface between biology and mineralogy. In all of these studies, we can expect to see the use of ever more-sophisticated photon probes.

Arrival at this point in my career has been a team effort. My colleagues at Caltech provide an intellectually rich and stimulating environment. I have been particularly blessed with excellent students and outstanding postdocs and visitors from around the world. The many collaborators with whom we have worked have likewise been a source of stimulation and source of intellectual growth. I was also fortunate to have had a wife who actually enjoyed spending a significant proportion of our vacations exploring mine dumps and assorted small pits in the ground. Many people throughout my life encouraged me in many ways. At first, gifts of chemicals nurtured my budding interest in science, and later, gifts of minerals became important sources of materials for research and study. To all of you that have been beside me on this journey, I extend my sincere appreciation and look forward to good times ahead.