

Presentation of the Roebling Medal of the Mineralogical Society of America for 1988 to Julian R. Goldsmith

ROBERT C. NEWTON

Department of Geophysical Sciences, University of Chicago, Chicago, Illinois 60637, U.S.A.

It is my great privilege to present Julian Goldsmith for the Roebling Medal. This award, the highest bestowed by the Mineralogical Society of America, customarily honors a long career of research marked by contributions of great importance. My task as a citator is, in this respect, straightforward. It would be difficult to identify a body of accomplishments of one mineralogist that is of greater importance than Julian's work. The problem our medalist presents today, however, is that he has fundamental research currently in progress, the potential importance of which compares with his monumental past accomplishments, and some aspects of it are, in fact, controversial. It is this recent work that I feel must be emphasized, even though it complicates my task. A scientist's career is most conveniently summarized in retrospect, at or near retirement from active research. If only Julian were scaling down his research toward a graceful retirement, my job would be much easier.

In order to describe these recent events, some historical background is necessary. Three decades ago and more, Julian Goldsmith and Fritz Laves first defined crystallographically the polymorphism of alkali feldspar. They showed that it is possible to convert low-state, or ordered, albite and microcline to the high, or disordered states, by long annealing at very high temperatures, near their melting points. Although they could not further emulate nature by performing the reverse, or ordering, experiment, they logically outlined the probable topologies of the high and low alkali feldspar solid-solution diagram. These new concepts set the stage for most of the experimental and theoretical work that was to follow (the feldspars, which account for fifty percent of the Earth's crust, were bound to become a primary target of experimentalists). The temperature range of structural inversion and the possible stabilities of intermediate states of ordering remained undetermined until a few years ago.

Analogous problems of solid solution and cation ordering and their complex interactions exist in the carbonate minerals. Julian had long been fascinated with the great range of solid solutions in these minerals, and he realized that some low-temperature processes in nature produce hugely metastable solid solutions. Creatures like the spiny sea urchin, for instance, don't care a whit about equilibrium thermodynamics—some of them make shells of calcium carbonate (calcite) with large, metastable amounts of magnesium carbonate in solid solution. Julian found that their shells can be decomposed artificially to a mixture of dolomite (nearly stoichiometric Ca-Mg carbonate) and calcite, at elevated temperatures. Julian's

and Don Graf's experimental determination of the temperature dependence of the solid solution between calcite and dolomite appeared simultaneously with the independent study of Ian Harker and Frank Tuttle. Both studies found that the equilibrium solubility of Mg in calcite is indeed vanishingly small at ocean-water temperatures. The little sea urchin illustrates Goldsmith's "simplicity" principle, that nature is full of low-temperature metastability that mimics high-temperature disorder and solid solutions.

Julian wanted to try to disorder dolomite experimentally and knew that this would require temperatures above 1000 °C and pressures of many kilobars to suppress the great tendency toward decarbonation at those temperatures. In the summers of 1958 to 1960, he went to UCLA to work with Hugh Heard and his "Mighty Teacart" gas apparatus. I was a graduate student there, a circumstance not unrelated to my eventual migration to Chicago. Together, Goldsmith and Heard climbed to the top of the calcite-dolomite solvus, where, near 1100 °C, dolomite is disordered in its Ca and Mg arrangement and becomes a completely continuous solid solution with calcite. Their classic diagram is a model of phase-equilibrium research and still often cited: it remains a cornerstone of discussions of the interaction of disordering and solid solution in general and calcite-dolomite geothermometry in particular.

During this period, Julian was adding Fe and Mn to his carbonate entourage. With Don Graf and others, he produced what may be the first experimental studies of ternary solid solution in minerals. These diagrams, though thirty years old, are still much used in discussions of carbonate stability in nature.

Julian has said that he doesn't think that he ever pioneered anything. If this is true, it is indeed strange that he still gets reprint requests for papers published in the late 1940s and early 1950s. It's good to know that some people are cognizant of original sources. Work as fundamental as Julian's on feldspars and carbonates tends to merge with time into the set of axioms and truisms that are taken for granted as starting points.

Scapolite is a mineral series composed of major feldspar and carbonate component molecules. With Julian's background in those two mineral groups, it seems natural that he would get interested in scapolite. I had the pleasure of working with Julian about ten years ago on this interesting mineral series. We showed that meionite, the common carbonate scapolite of deep-crustal rocks, is a very refractory mineral at elevated pressures: it has nearly

the same pressure-temperature stability as anorthite feldspar and can be a stable storage site for carbon dioxide in deep-seated rocks.

This preamble brings me to the most important point, namely, current events. The waves of surprise, and, it must be said, of disbelief in some quarters, have scarcely subsided since Julian announced his experimental determination of the stability of intermediate structural states of sodium feldspar (albite). He purported to be able to reverse at will the degree of ordering of those recalcitrant Al and Si atoms that have driven experimental petrologists to despair and to have done so in quite modest laboratory times in an unbelievably low temperature range—600 to 800 °C. A simple calculation of the rate of the disordering reaction based upon known activation energies and bond energies might cause an experimenter to abandon the idea of reversing the order-disorder reaction over small temperature ranges and small differences in structural states. Earlier experiments by others had met with some success in synthesizing an ordered albite with the use of alkaline solutions at high pressures, but only at temperatures several hundred degrees below where natural low albite could be synthetically disordered. Julian's experiments, in contrast, were carried out at high pressures in stringently dried and sealed containers, deliberately excluding water, the most potent mineralizing flux for silicates. I must confess to having had doubts initially about Julian's claims, and I'm sure I wasn't the only one. Some sort of magic was necessary to overcome the great kinetic barriers, and mere dry pressure just couldn't be the answer. Some extremely potent fluxing agent must have operated in his experiments.

Julian's next set of experiments, designed to identify the mysterious flux, reminds me of the classic experiments of Michael Faraday in identifying the properties of electromagnetism. Julian reasoned that only one substance could have penetrated his sealed platinum sample containers, namely monatomic hydrogen. He further guessed that the hydrogen was released by dissociation of trace amounts of water in the sodium chloride pressure-transmitting medium. He systematically designed and carried out experiments to shield his charges from hydrogen, both by an impermeable molten glass envelope and by screens of hydrogen-getting substances such as hematite. The great decrease he observed in the order-disorder reaction rates in albite under these hydrogen-poor experimental conditions is dramatic proof that hydrogen is indeed the powerful and mysterious flux.

Just how hydrogen does the job, and how it cooperates with high pressures, are still important problems to be worked out. Julian thinks that hydrogen ions (protons) stream through the platinum envelopes and create transient hydroxyl groups in the feldspar. The greater degree of dissociation of H₂O at high pressures tends to promote this effect, but some other factor must operate as well.

Julian believes that the hydroxyl groups can cause a transient recoordination of aluminum with oxygen from the normal fourfold arrangement to an activated complex which includes five or six oxygens. Concentration of this activated complex, and hence, of its effectiveness in promoting diffusion, would certainly be strongly favored by high pressures. Quantitative analysis of the effect of pressure on the stability of transient hydroxyl and transient recoordination will be a tough problem for the most gifted theorists. Julian's detailed rate-of-reaction studies on disordering in albite and in potassium feldspar, published this year, will figure prominently in the ultimate clarification of one of the strangest, and, indeed, one of the most important, effects yet discovered in experimental research on minerals.

A word is in order about the importance of proton-accelerated reaction rates in nature. We can expect, in light of Julian's findings, that things happen much faster than we used to think possible—rates of plastic deformation, recrystallization, equilibration of assemblages, and attainment of equilibrium ordering states are likely to be high even in the driest and most refractory regimes like the lower crust and upper mantle. This is good news for experimentalists like me, who are always hoping that equilibrium properties, which are easier to define experimentally than rate properties, frequently apply to natural processes in rocks.

Julian and his colleagues at Chicago have been compiling a definitive data set of experimental oxygen-isotope fractionation among minerals. Partitioning of the three stable isotopes is potentially one of the most important monitors of natural processes, and a valuable geothermometer. The latest breakthrough is isotopic equilibration of silicate minerals with carbonates. I don't exactly know how Julian thought of this. Perhaps our work on carbonate-silicate minerals suggested it. He got the idea before he knew about the role of hydrogen, and it still isn't clear if the carbonates donate hydrogen from trace moisture content to accelerate oxygen diffusion in the silicates. At any rate, carbonate works better than high-pressure water, the effective but sometimes erratic exchange medium used in many previous studies. Petrologists can expect some very useful data as these oxygen-isotope data approach publication.

Perhaps the difficulty of my citator's task is now becoming apparent. I've tried to summarize a career that is still in full swing. The open-ended nature of this account must seem like a citation for the MSA award, which Julian won many years ago. I feel that it is particularly appropriate that the Roebling Medal recognizes, in the present award, ongoing research as well as past research. The award today honors a long and distinguished career, current accomplishments, and important contributions yet to be published. I am indeed proud to present such a dynamic, as well as illustrious, awardee.