

## Presentation of the 2013 Roebling Medal of the Mineralogical Society of America to Frank C. Hawthorne

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I am pleased to introduce Frank C. Hawthorne as the recipient of the 2013 Roebling medal. Frank is a colleague and friend of some 31 years, someone with whom I have shared a great deal, and someone from whom I have learned a great deal. Frank was an undergraduate in pure geology at the Royal School of Mines, Imperial College, London, and did his Ph.D. in geology at McMaster University. From there, he went to the University of Manitoba for a post-doctoral fellowship in 1973, became a Research Associate in 1975, a federally funded University Research Fellow in 1980, an Associate Professor in 1984, Distinguished Professor in 1997, and was appointed a Canada Research Chair in Crystallography and Mineralogy in 2001, a position that he still holds. I arrived at the University of Manitoba in 1983 to set up the geochemistry laboratories. Frank was responsible for the MAC 5 electron microprobe and had just been awarded funds to buy a single-crystal diffractometer, the first in a geology department in Canada, so we connected quickly over the temperamental behavior of instrumentation and the problems of laboratory space, issues that still concern/annoy us both today.

Frank did his Ph.D. on the crystal chemistry of the amphiboles using a combination of single-crystal X-ray and neutron crystal-structure refinement and Mössbauer spectroscopy, and he has maintained an interest in this area through his whole career. In 1983, he began a collaboration with the Crystallography Group in Pavia: Roberta Oberti, Luciano Ungaretti, and Giuseppe Rossi. This led to his spending a total of four years in Italy, the publication of numerous papers on the crystal chemistry of amphiboles, and an MSA Short Course on Amphiboles in Rome in 2007. The complexities of site populations in amphiboles, together with the occurrence of variable H, Li, and  $\text{Fe}^{3+}/\text{Fe}^{\text{tot}}$ , encouraged his interest in spectroscopic methods and the idea of complementary instrumental techniques, and he rapidly became expert in IR, Mössbauer, MAS NMR, and XP spectroscopies, all used on materials previously characterized by crystal-structure refinement. This eventually led to him organizing the 1988 MSA Short Course: *Spectroscopic Methods in Mineralogy and Geology*. In 1996, careful spectroscopic work led to the detection of short-range-ordered arrangements in amphiboles. Formation of the Amphibole Consortium (Giancarlo Della Ventura, Mati Raudsepp, Mark Welch, and Frank) led to the extensive discovery and characterization of short-range-ordered arrangements in a wide variety of complex amphiboles through a combination of Rietveld structure-refinement and IR spectroscopy. Frank derived a local form of Bond-Valence Theory (i.e., NOT a mean-field approach) and showed that this can be used to predict patterns of SRO in amphiboles and other complex minerals.

Light lithophile elements (LLEs) can be important variable components in many rock-forming and accessory minerals that

were thought either to be free of LLEs, or to contain stoichiometrically fixed amounts of these components. With his students and colleagues, Frank pioneered the systematic examination of these types of crystal-chemical issues using a combination of SREF (Site-occupancy REFinement), SIMS (Secondary-Ion Mass Spectrometry), HLE (Hydrogen-Line Extraction), IR spectroscopy, and the local form of bond-valence theory. Of particular interest are the occurrence and role of variable Li, Ti, and H in amphiboles, variable Li and H in staurolite and tourmaline, variable B and H in vesuvianite and kornorupine. This work has resulted in much improved understanding of the crystal chemistry of these minerals, and more realistic activity models for thermodynamic treatment.

While a graduate student at McMaster University, Frank became close colleagues with David Brown and Bob Shannon at a time when bond-valence theory was being developed, and he has been involved with this area ever since. In the middle 1970s, stimulated by direct interaction with Petr Černý and Bob Ferguson, and by the papers of Paul B. Moore, Frank began to be interested in a wide range of complex minerals. This led to an interest in the general architecture of crystal-structure arrangements, and he began to use graph theory and combinatorial topology to examine a priori approaches to structural arrangements. He recognized topological isomerism as distinct from chemical isomerism, and combined these ideas with some extensions of bond-valence theory to produce a quantitative but very simple (back-of-an-envelope) theory for mineral stability. He provided the theoretical basis for structural hierarchies and has developed these for several major groups of minerals (borates, sulfates, phosphates, aluminofluorides, vanadates, beryllates). Brown (2002: Bond-Valence Theory) christened Hawthorne's proposal *The Structural Hierarchy Hypothesis* and this approach is now in general use by others to organize and understand minerals as diverse as uranium oxysalts and minerals containing anion-centered tetrahedra. This hierarchical approach formed a necessary basis for Frank's further work in understanding mineral occurrences in complex non-equilibrium environments with large numbers of phases. Before this work, the electroneutrality requirement was the only known constraint on the chemical composition of minerals. He showed that bond-valence theory can work at a local scale and is extremely effective in characterizing short-range order in complex rock-forming minerals, and together with Michael Schindler, has also developed a mean-field approach whereby the factors affecting the chemical compositions of very complicated hydrated-oxysalt minerals can be understood. This bond-topological approach has allowed several other constraints on possible chemical compositions to be recognized, to the extent that one can now predict many aspects

of the structures and chemical formulae of complex minerals that were hitherto mysterious: coordination numbers, types and amounts of univalent and divalent cations, and the amount of “water of hydration.” These advances have immensely improved our general understanding of mineral chemistry and the factors that affect the structural architecture and chemical compositions of minerals.

In the late 1980s, Frank was co-supervising a grad student in physics who was building a high-energy (40 MeV) proton microprobe. This prompted our first intellectual interaction and we became involved in a lot of interesting work: microbeam analysis of *K*-lines of all elements of the periodic table, the development of Proton-Activation Analysis, and the first use of fractal dimensions to characterize oscillatory zoning patterns in crystals.

Hydrogen was long considered as a fairly unimportant component in minerals, particularly when present as “water of hydration”. In 1992, Frank changed this view by showing that H controls the type of structure in minerals. Because of its very polar nature, H can terminate strong linkage in particular directions in a structure, giving rise to cluster, chain, sheet, and framework polymerizations. This accounts for the large-scale distribution of minerals within the Earth. Degassing throughout the Earth’s history has caused H to concentrate in the crust and atmosphere where it can cause structural diversity in minerals crystallizing in these environments. Minerals forming in the core,

mantle, and deep crust do not incorporate much H and generally crystallize as frameworks. Minerals forming in the shallow crust or at the Earth’s surface have cluster, chain, sheet, and framework structures in response to the H incorporated. Rarely has work at the atomic level unified such wide and large-scale diversity in the Earth sciences.

In his career, Frank has published over 600 refereed papers in scientific journals and 30 chapters in books. He was listed by Thomson Scientific as the World’s most-cited Geoscientist of the Decade 1996–2007 and was listed by *SCIENCEWATCH*, the journal of The Institute of Scientific Information, as the World’s most-cited Mineralogist of the Decade 1990–2000 and the World’s third most-cited Geologist of the Decade 1990–2000. Throughout his career, Frank has addressed the most fundamental problems in Mineralogy and, with his combination of theoretical insight, experimental imagination, and analytical expertise, he has essentially re-written much of our understanding of the structure and chemistry of minerals. He is an extremely imaginative scientist and continually introduces new ideas and approaches across a wide range of Mineralogy; he refuses to gloss over difficulties, to accept “woolly” solutions to difficult problems, or to publish before he feels that he understands the problem at hand. These are the reasons why he has made such fundamental and widespread contributions to mineralogy, and these are the reasons why he has been awarded the Roebling Medal.