CITATION FOR CHEMICAL BREAKTHROUGH AWARD: MENDELEEV'S PERIODIC SYSTEM OF THE ELEMENTS

David E. Lewis, Department of Chemistry, University of Wisconsin-Eau Claire, Eau Claire, WI 54703-4004, lewisd@uwec.edu

In 2012, the Division of the History of Chemistry (HIST) of the American Chemical Society's Citation for Chemical Breakthrough award was given to St. Petersburg State University for Dmitrii Mendeleev's publication "Ueber die Beziehungen der Eigenschaften zu den Atomgewichgten der Elemente" (1, 2), which introduced was is now known as the Periodic Table of the Elements to readers in western Europe. One key element of the Citation award requires that the paper honored be the *breakthrough* paper, but exactly what that demands is left to the reviewers to judge (3). Historically, the breakthrough paper has not always been the *first* paper in which the breakthrough is announced, but is rather the most influential paper—the one that had the greatest impact in the scientific community, and thus was far more than an interesting innovation but rather a true scientific "breakthrough" (4). In the case of Mendeleev's Table, there are six reasonable candidates for the breakthrough publication:

- Mendeleev's *Osnovy Khimii* [*Elements of Chemistry*], which was published in February, 1869 (5), and particularly the periodic arrangement of the elements contained therein;
- the German abstract of the same section of *Osnovy Khimii*, published in the *Zeitschrift für Chemie* also published in 1869 (2);
- the 1869 paper in the *Zhurnal Russkago Fiziko-Khimicheskago Obshchestva*, actually presented to the Academy by Mendeleev's friend, Nikolai Aleksandrovich Menshutkin, in which the relevant section of the *Osnovy* was described (6);
- the 1871 paper (7) in the *Zhurnal*, in which the case for the periodic system is laid out much more clearly, with the full predictions of the existence and properties of the three as-yet-undiscovered elements, eka-boron (scandium), eka-aluminum (gallium) and eka-silicon (germanium), and which included corrections to the earlier paper;
- the 1872 paper (8) in the Supplement to *Liebigs Annalen der Chemie*, which is a German translation of the 1871 *Zhurnal* paper; and
- Mendeleev's 1871 paper (9) in the *Berichte der deutschen chemischen Gesellschaft*, in which he answers questions about his periodic system raised by other authors, Lothar Meyer among them.

If we examine each of the journal articles in turn, beginning with the 1869 *Zhurnal* paper (which contained essentially the same periodic table as that proposed in the *Osnovy Khimii*), we see the gradual evolution of the periodic table to the final form proposed by Mendeleev. In the 1869 paper, Mendeleev had already begun the

process that was to make his the dominant name in the development of the periodic system. In the *Zhurnal* paper, Mendeleev went to great lengths to show the logic by which he had arrived at his system of the elements, which is shown in Figure 1. It already contained the two major intuitive leaps that have come to characterize his periodic system: First, four missing elements (scandium, predicted atomic weight 45; gallium, predicted atomic weight 68; germanium, predicted atomic weight 70; and hafnium—the one usually forgotten—predicted atomic weight 180) are already specified by placeholders (question marks) with appropriate approximate atomic masses; and second, tellurium and iodine have been placed where their chemical properties require, making the chemistry of an element the dominant factor in determining its place in the Table. One should note that Mendeleev's decision appears to be predicated, in part, on the possibility that the atomic weight of tellurium is in error.

However, the table also contains errors that were later corrected: Gold is placed in Group IIIA, and lead in Group IIA presumably based on the Au (III) oxidation state, which is much more common than the Au (I) oxidation state, and the Pb (II) oxidation state, which is much more prevalent than the Pb (IV) oxidation state. Thallium, on the other hand, is placed in Group IA for the same reasons. It is interesting to note that Mendeleev placed these elements in positions now occupied by radioactive elements unknown at the time. Incorrect atomic weights also played their part: the atomic weights of uranium (116 instead of 238), thorium (118 instead of 232) and indium (75.6 instead of 114.8) are all incorrect, and led to errors in placement.

			Ti = 50	Zr = 90	? = 180		
			V = 51	Nb = 94	Ta = 182		
			Cr = 52	Mo = 96	W = 186		
			Mn = 55	Rh = 104,4	Pt = 197,4		
			Fe = 56	Ru = 104,4	Ir = 198		
		Ni =	Co = 59	Pd = 106,6	Os = 199		
H = 1			Cu = 63,4	Ag = 108	Hg = 200		
	Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112			
	B = 11	Al = 27,4	? = 68	Ur = 116	Au = 197?		
	C = 12	Si = 28	? = 70	Sn = 118			
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210?		
	O = 16	S = 32	Se = 79,4	Te = 128?			
	F = 19	Cl = 35,5	Br = 80	J = 127			
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204		
		Ca = 40	Sr = 87,6	Ba = 137	Pb = 207		
		? = 45	Ce = 92				
		?Er = 56	La = 94				
		?Yt = 60	Di = 95				
		?In = 75,6	Th = 118?				

Figure 1. *The periodic system of the elements as it appeared in Mendeleev's 1869 article in the* Zeitschrift für Chemie. *It is essentially the same as the table that appeared in the* Zhurnal Russkago Fiziko-Khimicheskago Obshchestva *earlier the same year.*

The 1869 *Zhurnal* paper is clearly the heart and soul of the periodic system, but since it was published in Russian, its circulation would not have raised it to the level of being the breakthrough paper. This was fulfilled by the 1869 German abstract, in the *Zeitschrift*, with its wider circulation, and more diverse readership.

The 1871 paper in the *Berichte* is a polemical response to comments by others made on the basis of the German abstract, instead of the full paper, as is clear from the opening sentence: "Since the observations of HH. Gerstl, Blomstrand, Lothar Meyer, and Baumhauer on the subject of my proposed system of elements are made on the basis of the Referate***) of the full paper published in Russian, allow me to add some explanation." In the footnote referred to in this sentence, Mendeleev then sets out the chronology of his papers on his Periodic System of the Elements. The fact that Mendeleev's claims had already attracted such attention from German-reading chemists certainly bolsters the credentials of the *Zeitschrift* paper to be the breakthrough paper. Other than that, the *Berichte* paper itself contains no new information, but is largely a defense of Mendeleev's claims to priority over those of Odling and Meyer.

The remaining two papers, the 1871 publication in the *Zhurnal*, and its 1872 translation into German, published in the Supplement to the *Annalen* are both much more substantial papers than the original 1869 publication. The *Zhurnal* paper is over twice as long as the original, and, in dramatic contrast to the brevity of the two-page summary in the *Zeitschrift,* the *Annalen* paper was substantial: in its 96 pages, it contained a detailed development of the concepts underlying the periodic law, setting out explicitly the predicted properties of the three elements that gave credibility to his system as they were discovered: eka-boron (Sc), eka-aluminum (Ga) and eka-silicon (Ge). Mendeleev's thinking is set out in this paper in a highly logical fashion, and his arguments are both powerful and persuasive. At the same time, a number of errors in the original paper were corrected: the correct atomic weights for indium, uranium and thorium led to their placement being changed, as also happened for thallium, gold and lead, all of which were moved to their correct locations in the Table. Mendeleev did, however, pull back from his prediction of the existence of a new element below zirconium, and he replaced his predicted hafnium with lanthanum—the placement of the rare earth elements was problematic for Mendeleev in both forms of his periodic table, and was not cleared up until the work of Henry Gwyn Jeffries Moseley (10).

As intimated above, deciding which of these candidates is the breakthrough paper becomes a subjective call, made somewhat more so by the fact that three of them are in Russian, and all appeared before the corresponding German versions. Thus, if simple precedence in time is the determining factor, the 1869 *Zhurnal* paper should get the accolade. But, during the nineteenth century, German was the most authoritative language in science. Almost all Russian chemists could read and write German and French, and many (but not Mendeleev) could also read and write English. The reciprocal situation did not, however, hold: relatively few western European chemists could read Russian, a situation that still obtains today. Thus, because the first published paper detailing what later became known as the Periodic Law is written in Russian, which would undoubtedly have much reduced its impact outside of Russia.

A good example of the impact of this difference in language on the reception of a publication is provided by the Wolff-Kishner reduction. The first paper describing the decomposition of hydrazones by base was published—in Russian—by Nikolai Matveevich Kizhner in March, 1911, in the *Zhurnal Russkago Fiziko-Khimicheskago Obshchestva* (11); some eighteen months later, at the end of 1912, essentially the same reaction was published—in German—by Ludwig Wolff in *Liebigs Annalen* (12), without reference to Kizhner's earlier work. Kizhner's paper had also been abstracted, in German, into the *Zeitschrift für Chemie*, which is where Mendeleev's 1869 paper was also abstracted; the fact that Wolff did not refer to Kizhner's earlier work suggests that Wolff did not regularly read the *Zeitschrift*, and is probably indicative that the influence of this journal in western European chemistry had waned by that time. The effect of the language of publication, means that the reaction is known today in the west as the Wolff-Kishner reduction rather than the Kizhner-Wolff reduction (as it is known in Russia) because Wolff's paper, in German, was much more widely read by western chemists than Kizhner's, in Russian. This situation, also, may provide yet another example of where the "breakthrough" paper may not be the first paper published on the subject.

There appears to be little disagreement that the origins of Mendeleev's periodic table can be traced to his 1869 textbook *Osnovy Khimii*, and that during the writing of this treatise he came to the conviction that the periodicity he had observed was, in fact, both real, and useful. As is taught in many introductory chemistry textbooks, it was Mendeleev's leap of faith that there were elements not yet discovered, and his prediction of their existence and their properties—spectacularly confirmed as his predicted elements were discovered, one by one—that separated his predictions from those of Lothar Meyer (13) and John Alexander Reina Newlands (14). However, Mendeleev's textbook was written in Russian, and this reduces its claim to be the breakthrough publication for the concept of periodicity. Likewise, the 1869 publication in the *Zhurnal* likely had insufficient impact to qualify as the breakthrough paper. In fact, it has been argued by Gordin (15) that, at that point in time, Mendeleev himself had not grasped the epoch-making nature of his discovery, since he had his friend, Nikolai Aleksandrovich Menshutkin (1842-1907), deliver the paper to the Russian Physical-Chemical Society while he, himself, was inspecting cheese factories outside Moscow. Of course, one can also place the interpretation on events that Mendeleev did, in fact, fully realize the importance of his Periodic System, and chose to have his friend present the paper rather than delay its presentation until he could do so in person.

In similar fashion, Mendeleev's 1870 paper in the *Zhurnal* possesses all the hallmarks of the breakthrough paper—it clearly defines the underlying science, corrects some earlier mistakes, and makes the predictions that, when confirmed later, placed the periodic table of the elements on course to become one of the most widely-recognized scientific icons of modern times. But ... it was written in Russian, and that means that its dissemination in western Europe was limited. The language of publication thus becomes an automatic disqualifier for a paper to become the "breakthrough paper."

This analysis leaves us with the two German publications as the possibilities for the breakthrough paper. The earlier of the two is the brief, two-page abstract of the 1869 *Zhurnal* paper, and it appeared the same year in the *Zeitschrift für Chemie*. This journal had had a checkered history from its founding by Richard August Carl Emil Erlenmeyer, through its heyday when the editors were R. Fittig H. Hübner (both in Göttingen) and Friedrich Konrad Beilstein (Fëdor Fëdorovich Beil'shtein; like Mendelejeff, in St. Petersburg), to re-emergence in various guises over the next century and a half. Early on, it became an important western outlet for Russian chemists to publish original research papers—Butlerov published his version of structural theory (16) in the *Zeitschrift* at Erlenmeyer's urging—but this journal's influence fluctuated over time. Nevertheless, its abstracts of papers appearing in Russian became an important part of the dissemination of these papers to a wider audience. At the time that Mendeleev's paper was abstracted by the

Zeitschrift, one of the editors was Beilstein, who had become Professor of Chemistry, and Mendeleev's successor at the St. Petersburg Technological Institute, in 1865; Beilstein was a strong advocate of having his Russian colleagues publish their papers directly in the *Zeitschrift*. However, as noted above, despite the wider readership of the *Zeitschrift* by comparison with the *Zhurnal*, the question remains as to whether or not this paper satisfies the high-impact criterion.

For me, the answer to this question was provided by the 1871 paper in the *Berichte* (9), which was discussed above. In this polemical paper, Mendeleev addresses the questions raised by western chemists. To my mind, this adds unequivocal support to the claim of the 1869 *Zeitschrift* paper to be the breakthrough paper, since it had clearly attracted the attention of chemists, among them Lothar Meyer, who had been working on a similar arrangement of the elements. It is doubtful that a chemist of Meyer's standing would have commented on a paper in the *Zeitschrift* at this time had that paper not been, in his eyes, important enough to warrant comment. Whatever his reasons, Meyer's response, and those of his contemporaries in the west, clearly mark Mendeleev's paper in the *Zeitschrift* as a breakthrough development. But is it *the* breakthrough paper?

Which brings us to the 1872 paper in the Supplement to *Justus Liebigs Annalen der Chemie* (8). This paper, too, was a German translation (by Felix Wreden, or Feliks Romanovich Vreden, d. 1878) of the paper (7) that had already appeared in the *Zhurnal*, and the difficulty it presents is in terms of deciding whether it is a much stronger candidate for the breakthrough paper than the *Zeitschrift* paper. Certainly, *Justus Liebigs Annalen der Chemie* was the most established, and influential chemical journal in Europe by the middle of the nineteenth century, and papers published in it were both widely read and influential.

But the question remains, does the 1872 full paper deserve to be the award-winning paper? Despite its greater detail, and fewer errors, it appears that by the end of the nineteenth century, chemists had decided that Mendeleev's 1869 paper in the *Zeitschrift* should be the one credited with the discovery. Thus, although references to the 1872 paper continued, the periodic table itself was dated to 1869, which suggests that Mendeleev's contemporaries and their immediate successors made the decision that the 1869 *Zeitschrift* paper was the breakthrough publication. The reasons for this preference, particularly in light of the persistent references to the 1872 paper, are not clear.

It is interesting to examine how Mendeleev's Table is referred to around the turn of the twentieth century, by which time its validity had been established beyond doubt. In his 1913 textbook, "A New Era in Chemistry," (17) devoted to the rise of physical chemistry, Harry C. Jones makes the statement, "A generalization that fits the facts much better, was the periodic system of the Russian, Mendeléeff, and the German, Lothar Meyer. Mendeléeff in 1869[1] published his now famous periodic table of the elements, and Lothar Meyer discussed his arrangement of the elements, which was essentially the same as that of Mendeléeff, in 1870.[2]" It is interesting that the reference to Mendeleev's work here was not the *Zeitschrift* paper of 1869, but the *Annalen* Supplement paper of 1872, even though precedence was given to the 1869 date. In his 1911 "Theoretical Chemistry," (18) Nernst also uses 1869 as the date of origin of the Periodic Table, but he couples the names of Meyer and Mendeleev, and draws most of his material from Meyer's work.

In conclusion, based on the criteria for the award, and—an admittedly subjective—judgment of the available literature, I came to the conclusion that the 1869 *Zeitschrift* paper should be the one honored. This recommendation was accepted (see Figure 2), and the award plaque was formally presented on October 31, 2013 (Figure 3).

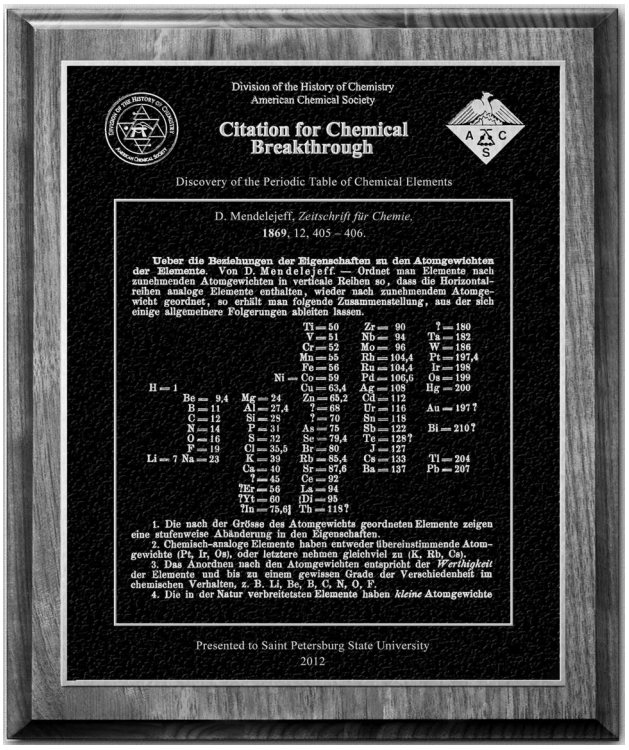

***Figure 2**. The plaque of the Citation for Chemical Breakthrough award to St. Petersburg State University.*

Figure 3. *The unveiling of the plaque of the Citation for Chemical Breakthrough award to St. Petersburg State University, adjacent to the statue of Mendeleev in the main hall of the historic Twelve Collegia building by the author (representing HIST, l) and Professor Sergey Sergeevich Ermakov (Vice-Dean of Chemistry, SPBU, r). Photograph courtesy of St. Petersburg State University.*

References and Notes

1. The transliteration from the Cyrillic alphabet presents a recurring problem for western writers, translators and publishers referring to Russian authors and articles. The exact transliteration used will depend on the writer, and on the language into which the article or name is translated or transliterated. In this paper, I have adhered to my previous practice of transliterating the Cyrillic using the BGN/PCGN romanization system for Russian as the most intuitive for English speakers. In this system, the name of the subject chemist becomes Mendeleev. In the German language publications, the transliteration, Mendelejeff, was used by Mendeleev himself as rendering the pronunciation of his name by German readers the closest to the Russian, but some early English transliterations (e.g. in the 1911 *Encyclopaedia Britannica*), his name is rendered as "Mendeléeff."
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3. J. I. Seeman, "HIST's Citation for Chemical Breakthrough Awards: The "First Paper" *or* the 'Breakthrough' Paper?" *Bull. Hist. Chem*., **2013**, *38*, 4-6.
4. The question of "first" or "breakthrough" for other CCB awards has been analyzed and reported on in other publications. See J. Gal, "Citation for Chemical Breakthrough Awards: Choosing Pasteur's Award-Winning Publication," *Bull. Hist. Chem.*, **2013**, *38*, 7-12; N. Craig, "Charles M. Hall's Persistent Quest of Patents for Refining Aluminum Metal by Electrolysis," *Bull. Hist. Chem.*, **2013**, *38*, 13-18.
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13. L. Meyer, "Die Natur der chemischen Elemente als Function ihrer Atomgewichte," *Ann. Chem. Pharm.* **1870**, *Suppl. 7*, 354-364. For a discussion of the development of the periodic system, and the priority debate that it engendered, see J. W. van Spronsen, "The priority conflict between Mendeleev and Meyer," *J. Chem. Educ.*, **1969**, *46*, 136-139.
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About the Author

David E. Lewis is Professor of Chemistry at the University of Wisconsin-Eau Claire. His research interests are in synthetic organic chemistry, with an emphasis on the synthesis of novel oral anticoagulants as adjuvants for warfarin. His interests in the history of chemistry are in the history of organic chemistry in Russia. He is a past Chair of HIST, a Fellow of the Royal Australian Chemical Institute, and earned the D.Sc. from Adelaide University in 2012.

Bulletin for the History of Chemistry Outstanding Paper Award for 2013

The Division of the History of Chemistry of the American Chemical Society is pleased to announce Professor Stephen J. Weininger as the winner of its 2013 Outstanding Paper Award. His paper, entitled "Chemistry for the 'Industrial Classes': Laboratory Instruction, Mass Education and Women's Experience in Mid-Western Land-Grant Colleges, 1870-1914", appeared in the *Bulletin for the History of Chemistry*, **2013**, *38(2)*, 97-108. On July 2, 1862, in the midst of the Civil War, President Abraham Lincoln signed the Land-Grant Colleges Act, commonly known as the Morrill Act after its principal sponsor. The Act's mission statement ensured that, because of their perceived centrality to agriculture, chemistry and other natural sciences would have a predominant place in the curriculum. Weininger's paper tracks each state's divergent ambitions by focusing on course curricula and catalog rhetoric relating to qualitative and quantitative analysis, bedrock courses for numerous majors that provided students with marketable skills. This paper is available for all to read at the HIST website: http://www.scs.illinois.edu/~mainzv/HIST/awards/paper.php

The 2013 winner, Stephen J. Weininger, was educated at Brooklyn College, CUNY and the University of Pennsylvania, where he received his Ph.D. in 1964. In 1965 he joined the Chemistry Department at the Worcester Polytechnic Institute and became Professor of Chemistry Emeritus in 2005. A former Chair of the HIST Division, he has published extensively in the areas of the history of physical organic chemistry, thermodynamics and chemical representation. Seeing the vital connection between chemistry and culture, he co-founded the Society for Literature and Science (SLS) in 1985, served as its president from 1987-89, and has given numerous talks in this area.

The Outstanding Paper Award is presented to the author of the best paper published in the *Bulletin for the History of Chemistry* during the previous three years, including the award year. The 2013 award is for a paper published in 2011, 2012, and 2013.