Rediscovery of the Elements

The Second Discovery of Vanadium

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This article follows the previous "Rediscovery" articles in the *Hexagon*, "Don Andrès Manuel del Río and Mexico,"[1] and "The Undiscovery of Vanadium."[2]

The Falun Mine. The "oldest copper mine in Sweden"[3] in Falun (Figure 1), 200 kilometers northwest of Stockholm (Figure 2), was first worked in the 13th century and ceased production in 1992.[4] Today this mine can be visited by tourists, who can don hardhats and descend by elevator to explore the huge caverns below, full of labyrinths adorned with waxen ferric sulfate stalactites and ancient wooden ladders. At the surface of the main shaft is a museum that reviews the history of Falun and Swedish mines. The Falun mine is now a national landmark and boasts a popular "virtual reality show."

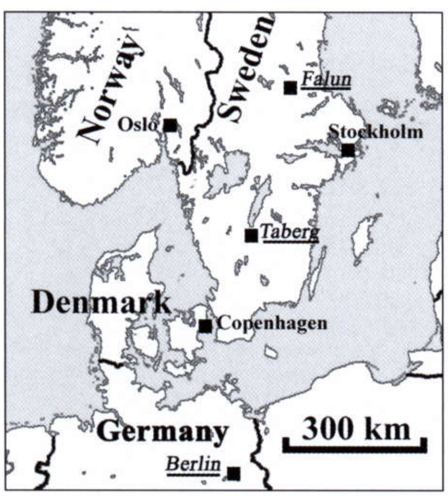

Figure 2. Important sites involved in the "second discovery" of vanadium included Falun, Taberg (10 kilometers south of Jönköping, not shown), and Berlin.

Figure 1. The famous copper mine in Falun, Sweden. On the elevator tower is the ancient alchemical symbol for copper.

Local myths relate that the mineral riches of Falun were first discovered when an errant goat named Kåre returned to its flock with red horns, dyed by iron-rich soil of the region. Copper itself was first mined by peasant farmers who discovered *Stora Kopparberget* (the "Great Copper Mountain") at Falun—a millennium ago at the end of the Viking Age. The area was a poor agricultural region with a seemingly inexhaustible supply of the highly valued commodity of copper, which was easy to transport and to coin. The village of Falun thrived, and a complex society of interdependent minehands, shops, smiths, and inns developed, overseen by the mayor in his ornate manor home. When a worker was killed in a mining accident, the widow was provided with a tavern to secure a livelihood for the family. Continued excavation created a cavern so huge that the ore-cart horses lived permanently underground; every so often these animals would be hauled to the surface to prevent permanent blindness. By 1641, when Falun gained its charter, it was already the second largest city in Sweden. Kopparberget provided much of the wealth necessary to support the vigorous foreign policy of Sweden during the 17th century.[4]

In 1774 Johann Gottlieb Gahn (Figure 3), master assayer at the Falun mine, discovered manganese by reducing *Braunstein* (German "brown stone," known today as pyrolusite, manganese oxide) with charcoal[5] in his "smithy" furnace (Figure 4).[6] It had been known for centuries that treatment of glass with braunstein (Swedish *brunsten*) would decolorize the product or impart a violet color to the final product. Because of its ability to "clean up" green or yellow glass, braunstein was known as *sapo vitri* (glass soap).[5] Gahn was a brilliant assayer who published little but was well respected in scientific Sweden; he was an expert in the use of the blowpipe and did much to promote the copper industry of Sweden. It is probable that Gahn was the first person to notice that a crystal retains its morphology when cleaved: when a sample of "dogtooth spar" (calcite, $CaCO_3$) fell accidentally and shattered, Gahn noticed that the rhomboid shape of the original crystal was retained in each of the fragments.[7] An exhibit on Gahn and his scientific equipment may be viewed in the Falun Mine Museum.

When Gottlieb Gahn died in 1818, his laboratory (Figure 4) was passed on to the newly formed Falun Mining School (Figure 5).[6] In 1831 Nils Sefström (Figure 6), a medical doctor who was the first Director at the School, discovered vanadium from some iron ore from Taberg, Sweden. Sefström was well known for his fine contributions to the iron industry,

Figure 3. Johann Gottlieb Gahn (1745–1818), master assayer at the Falun School of Mines (courtesy, E. B. Bergsman, ref. 6).

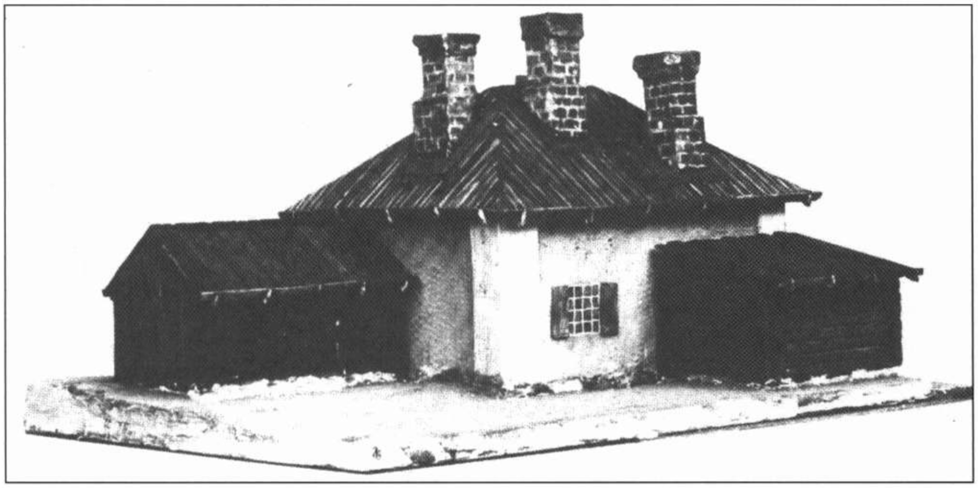

Figure 4. Gahn's laboratory, where he discovered manganese, was originally a blacksmith shop. (courtesy, E. B. Bergsman, ref. 6). A charcoal hopper extends to the left, a blast furnace to the right. This laboratory was taken down in 1840 to make room for the Mining School.

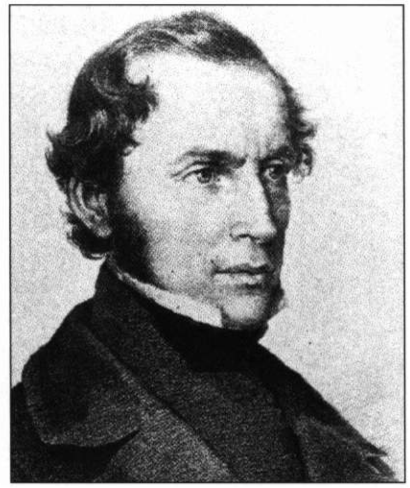

Figure 6. Nils Gabriel Sefström (1787–1845) discovered vanadium at the Falun Mining School (courtesy, E. B. Bergsman, ref. 6).

including new designs of iron manufacture and an account of history of iron mining in Sweden.[6]

Taberg's ore was valuable because it was very rich in iron (20–30%) and singularly free of harmful impurities that interfered with the smelting and forging of the final product. Sefström had been curious about an empirical test[8] developed for iron; it had been previously observed that muriatic acid (hydrochloric acid) dissolved iron to give a black powder (presumably iron phosphide) when the iron was "brittle." Sefström was surprised to find that the iron from Taberg was malleable and yet gave a *positive* "muriatic test." He investigated the black powder and found a new metal that behaved somewhat like chromium or uranium (both of which exhibited highly colored yellow salts), but which was clearly a new element. Berzelius in Stockholm checked the analysis, and the announcement was made in 1831 that a new element had been discovered.[9] They searched for a name beginning with "V" because most other letters of the alphabet had been taken. During his tests for chromium and uranium Sefström had produced salts and solutions having beautiful colors so they called it "Vanadium" after Freya ("Vanadis," the Scandinavian Goddess of Love and Fertility, renowned for her beauty).[8] The buildings of the Mining School in Falun (Figure 3), where the vanadium work was performed, were taken down in 1970 and now the site is occupied by a modern business and shopping area. (Figures 7,8).

Taberg, Sweden. Taberg Mountain juts 140 meters above the surrounding wooded plain (Figure 9), which the authors reached via a 3-hour freeway drive from Stockholm. A tourist bureau at the base of the mountain offered interesting literature and exhibits, and a road led to the summit, which sported a restaurant and a park. The view from the park included a

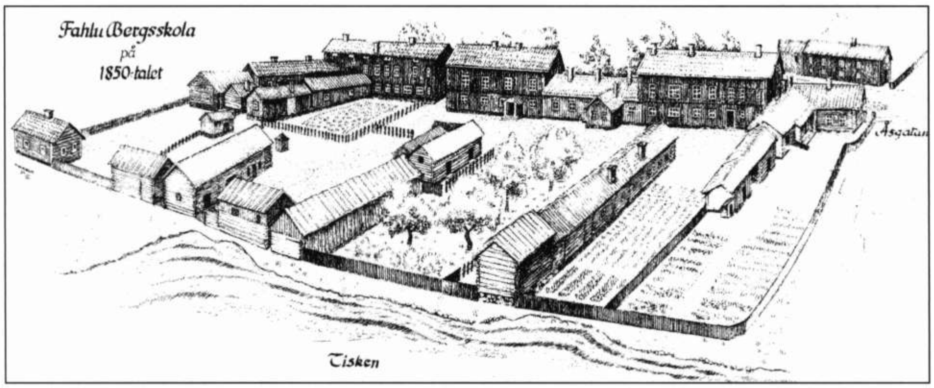

Figure 5. The Falun School of Mines (Fahlu Bergsskola) was created in 1819. This view, looking northeast, was sketched from the 1850s (courtesy, E. B. Bergsman, ref. 6). Åsgatan (see Figure 8) extends left to right, just beyond the line of main buildings. Sefström did his vanadium work in the main building to the right. Gahn's old "smithy" laboratory (now gone) had been 80 meters or so beyond the main line of buildings.

Figure 7. Looking southward, this modern office building was the site of Gahn's laboratory, at the corner of Bergskolegränd (running left and right) and Trotzgatan (running up the hill, diagonally right). Behind the office building is Åsgatan with its line of shops, where Sefström's laboratory was located.

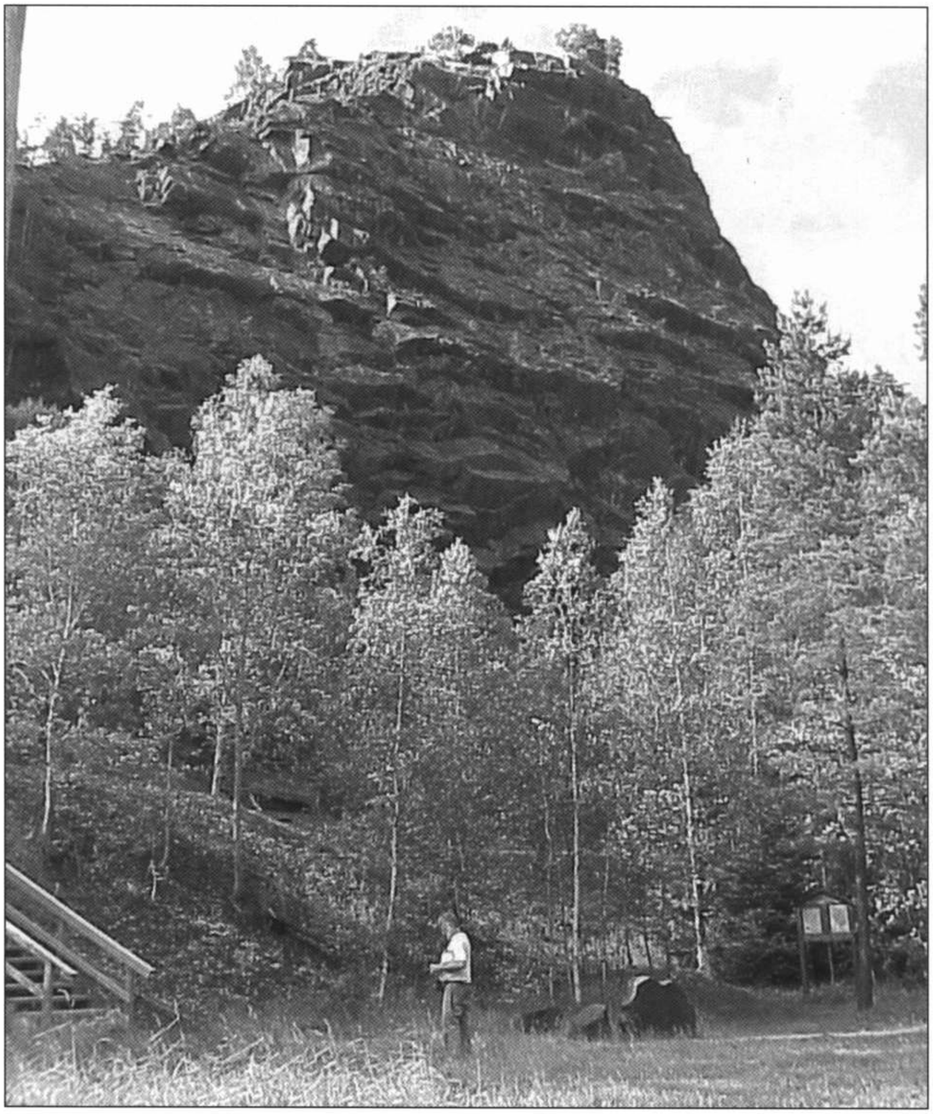

Figure 9. Taberg Mountain (N 57° 40.73, E 14° 04.93) is 10 kilometers south of Jönköping, Småland, which is connected by expressway to Stockholm, 300 kilometers to the northeast. At the summit can be seen a restaurant; about the base are scattered tons of debris broken from the dark cliffs.

beautiful panorama of the countryside, and in the center of the park was a huge cavity that had been excavated by miners since the 1500s.

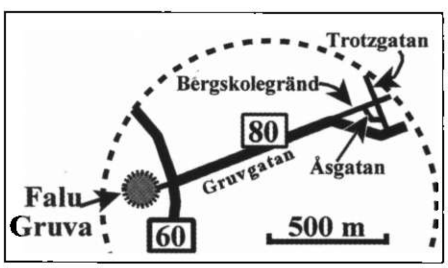

Figure 8. Gruvgatan ("Mine Street") runs from Falu Gruva ("Falun Mine," N 60° 36.01, E 15° 36.95) to the center of town where it becomes Bergskolegränd. At the south corner of Trotzgatan and Bergskolegränd was located Gahn's laboratory (N 60° 36.35, E 15° 38.10). Sefström's laboratory was located at the crook of Åsgatan (N 60° 36.31, E 15° 38.10).

The base of the mountain was strewn with talus slopes of this mineral broken off the black cliffs (Figure 9). The most fascinating aspect of Taberg was its unique composition—the entire mountain was composed of magnetite (Note 1). The unusual chemistry of the soil gives rise to unusual lichens, mosses, and other plants, which led Carl Linnaeus to visit in 1741. Strolling about the magnetic mountain, we found that magnetic compasses were ineffective, and intriguing demonstrations could be performed (Figure 10).

Wöhler's Discovery that del Río's *Erythronium* Was Identical to Vanadium. Friedrich Wöhler (1800–1882, Figure 11), fresh from his studies with Berzelius in Stockholm (1823–1824), made several important chemical discoveries at the Städtische Gewerbeschule [Municipal Technical School] in Berlin (Figures 12,13).[10] Here, in 1828, Wöhler was the first to synthesize urea from an inorganic salt, thus disproving the "vital theory" of organic compounds.[11] At this school he also prepared metallic aluminum, beryllium, and yttrium.[12] He narrowly missed the "second" discovery of vanadium by reinvestigating del Río's plomo pardo[1] supplied by Humboldt, who had brought a sample to Berlin in 1805.[13] Unfortunately, Wöhler had been delayed in his research because of health problems. After hearing of the Scandinavian discovery, the chagrined Wöhler cried, "I was a jackass [*Ich war ein Esel*] not to have discovered it 2 years earlier;"[14] Berzelius consoled Wöhler, saying that "it required more genius to synthesize urea than to discover ten new elements."[15] Wöhler procured a sample of Swedish vanadium and verified it was identical to the *plomo pardo* element that del Río had named erythronium.[13]

Figure 10. The entire Taberg Mountain is magnetic, composed of a form of magnetite (Fe_3O_4). Here, a rare earth magnet easily holds up one of the shards broken off the cliff.

Figure 11. This statue of Friedrich Wöhler stands at Wöhler Platz, Göttingen, Germany (N 51° 31.81, E 09° 56.17) between the former site of Wöhler's former laboratory (right, out of view) and the building where Friedrich Stromeyer discovered cadmium in 1817 (left, out of view).

Figure 12. The Technical school in Berlin, where Wöhler resided and worked during the period 1825–1831 (12 Niederwallstraße, N 52° 30.74, E 13° 23.97), is where he proved that urea could be produced synthetically by the isomerization of ammonium isocyanate (courtesy, H.W. Roesky and G. Beer, Georg-August-Universität, Göttingen, Germany).

In Europe, when Humboldt realized the truth about *plomo pardo,* he addressed[13] the Institut de France in February 2, 1831, in an attempt to remedy the error of Collet-Descotils, who three decades earlier had misidentified vanadium as chromium.[2] Five days later Berzelius publicly recognized in a letter to the Institut[13] and in a prompt publication[16] that del Río in fact made the original discovery of the new element. Now living temporarily in the United States (Note 2), del Río heard of the work of Sefström and Berzelius, and he passionately argued for recognition of his claim;[13] suggestions were made in the United States that the element be called not vanadium, but instead "zimapanium," or "-riom," or "-rionium."[17] "European monopolists have not always appeared solicitous to sustain the merit of discoveries effected in the Americas," del Río bitterly complained.[18] "Had Del Rio [sic] been in Europe, this matter would have been properly arranged long ago," the geologist Featherstonhaugh (Note 2) pointed out.[18] However, the Atlantic Ocean was too large a barrier in the early 1800s to allow an easy meeting of cultures and minds. Some in the Swedish and the German scientific communities might be willing to reconsider setting the record straight,[13, 19] but the issue was not considered important by others.

Should "Vanadium" Be Renamed "Erythronium"?

Two centuries later, it is now accepted that del Río should be given credit for discovery of vanadium.[19] Since the principle has long been adopted that the person who first discovers an element should be given the right to name it,[20] in 1947 two Mexican chemists proposed that the name "erythronium" should retroactively substitute "vanadium."[21] The timing of this suggestion was appropriate. During the 1940s the rash of discoveries of the artificial elements prompted a lively discussion of the criteria needed to establish the claim of discovery and the priority to name new elements.[22] It is a miscarriage of justice that the response to the 1947 Mexican article—a brief addendum to the article written by F. A. Paneth—was a rejection based on the false assertion that del Río relinquished all claim to the discovery of the new element[23] (Note 3). Unfortunately, the chemical community has historically resisted a return to an earlier name, even after it has been determined that the original discoverer should be given credit—examples include not only erythronium/vanadium, but also columbium/niobium,[24] and possibly casseiopium/lutetium.[22,24] Furthermore, there no longer exists any agency which can officially change the names for the natural elements:[25] it has long been stipulated by the IUPAC that, in the arena of the nomenclature of elements, it deals only with new, artificial elements.[26] It is unfortunate that it is too late to heed the plea of Featherstonhaugh:[27] "We believe that the tree of knowledge flourishes most, where the love of justice is strong...If we would have truth, we must plant justice...it would cheer the declining days...of the venerable Del Rio [*sic*], to learn that men have done that justice to his name, which fortune has never done to his merits."

Acknowledgments

The authors are indebted to Börge Bergsman of Falun, Sweden, the author of reference 7 and an expert on the history of the Falun area; the authors spent a pleasant afternoon in his charming lakeside house in Falun, where he graciously shared much important information. Herbert W. Roesky and Günther Beer of the Institut für Anorganische Chemie der Georg-August-Universität in Göttingen, Germany, provided information about Friedrich Wöhlers' activities in Berlin; Dr. Beer generously provided time to show the Historical Museum at the University and important historical sites in Göttingen. Dr. Lyman Caswell, Professor Emeritus of Texas Woman's University, Denton TX, is particularly recognized for his continuing help and suggestions during these "Discovery" articles on vanadium.

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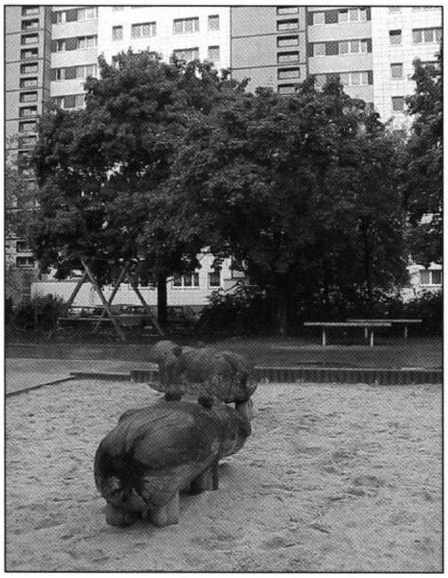

Figure 13. Apartments now stand on 12 Niederwallstraße. In the foreground is a children's playground with carved wood animals. Many of Berlin's historical buildings were destroyed in the devastation of World War II.

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Notes

Note 1. The 1.2 million-year-old geological formation at Taberg is an iron-titanium-vanadium deposit covering an area of 1 x 0.5 kilometers, extending to a depth of at least 500 meters. The unique composition is magnetite (Fe_3O_4) with small amounts of titanium (<5%) and vanadium (<1%), admixed with olivine (ferrous silicate).

Note 2. Upon the independence of Mexico, all Spanish-born residents were forced to leave Mexico; del Río moved to Philadelphia in 1829 where he was taken under the wing of the geologist George W. Featherstonhaugh. The tenure of del Río in Philadelphia lasted six years, when he convinced the Mexican government that "Mexico was his true country" and that he should be permitted to return.[13] Featherstonhaugh (1780–1866), a polymath of incredible versatility, was born in London and educated at Oxford. Traveling to the United States (1806) he engaged in agricultural research; railroad development; literary works (translation of Cicero and writing his own plays); editorship (founding the *Monthly American Journal of Geology and Natural Science*); and geological surveys of the western country (as the first United States Geologist). Returning to England (1838) he was appointed British consul to France; published works on his travels and translations from Italian literature; and involved himself in invective criticism of the U.S. South (writing *Excursion Through the Slave States*).

Note 3. It was the contention of Paneth that del Río had irrevocably renounced his claim because del Río thought, even to his dying day, that he had been investigating not a new element, but chromium. The literature, however, utterly refutes this contention, on the basis of direct quotations from del Río.[13,17,18] Paneth never had official status on the IUPAC;[25] even though he voiced his opinions frequently on discoveries and nomenclature of new elements[22] and had a prestigious record of accounts of historical chemistry,[28] it was outrageous for him to claim to "speak in authority" on this topic. It appears, therefore, that not only the Atlantic Ocean, but also the Rio Grande, was a barrier to easy interchange between scientific minds.

Terri (Dular Clark) **CARNAVGO**, *Gamma '90*, is now a Principal Scientist and Coatings Program Manager with Armstrong World Industries, Building Products Division, in Lancaster, PA. Terri and her husband Larry have three children, 8, 6 and 2 years old.

Ryan **GOBBLE**, *Zeta '00*, a third-year medical student at Southern Illinois University School of Medicine, has been awarded an Alpha Omega Alpha (AOA) Student Research Fellowship for 2004. He is one of approximately 40 recipients nationally who is receiving the $3,000 award and the tenth consecutive AOA national fellowship winner at SIU. He also won the award in 2003. The purpose of the fellowship is to promote research among medical students. The award supports Gobble's project, which is looking at why the expression of a protein is severely suppressed in obstetrical complications like pre-eclampsia, one of the leading causes of maternal and fetal morbidity and mortality. The research is under the supervision of Donald S. Torry, Ph.D., associate professor of medical microbiology and immunology at SIU. Gobble is examining the genetic mechanisms that regulate the expression of placenta growth factor in trophoblast cells of the human placenta.

David and Leonie **LLOYD**, *Delta '95* and *Gamma Mu '97*, respectively, announce the birth of Agustín "Gus" Glenn Lloyd on May 5, 2004 at Barnes-Jewish Hospital in St. Louis. Gus weighed in at 4.875 kg (10 lbs 12 oz) and was 21 inches long. Agustín is a family name from Leonie's side of the family and Glenn is from our brother Glenn Kuhlman, *Delta '89*, who passed away in 2002. The young man even appears to be a red-head. Cards may be sent to Dave and Leonie Lloyd, 4011 Flad, St. Louis, MO 63110.

Sally B. **MITCHELL**, *Pi '80*, is profiled in the 2003 Annual Report of the American Chemical Society for her work with chemical education. She has been active with Science Olympiad, Kids in Chemistry program, Chemagination, Earth Day, and her home *Pi* chapter at Syracuse.

Hays **YOUNG**, *Gamma Beta '96*, finished his PhD in Biochemistry in January 2004. His area of study was asthma research.