

Rediscovery of the Elements

Riddarhyttan, Sweden

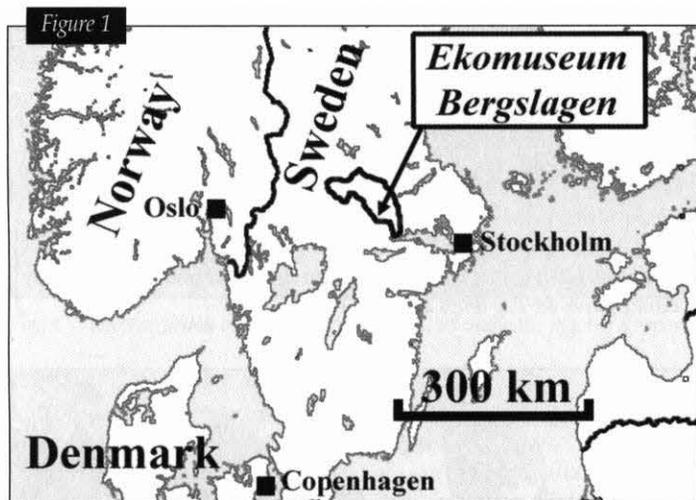


Figure 1. The Ekomuseum Bergslagen lies about 150 kilometers to the northwest of Stockholm, encompassing 7500 square kilometers. Riddarhyttan is located at the tip of the arrow, in the southern portion of the Bergslagen.

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The discovery of the seven ancient metals—gold, silver, copper, iron, tin, lead, and mercury—cannot be ascribed to any particular person, and even for the elements of the Medieval miners—bismuth, zinc, antimony, and arsenic—the reputed discoverers may be more legend than fact.¹ However, since Agricola² (Georg Bauer, Latinized to Georgius Agricola), 500 years ago, discoveries of new metals and semimetals are well documented. If we make a list of the countries in which these discoveries were made, Sweden easily heads the list. (Note 1) Lying on the geological Baltic shield, Sweden is blessed with the igneous and hydrothermal processes that have served as a

natural “chromatograph” to separate out hundreds of different minerals, some with unusual composition. Simultaneously, with educational centers at Stockholm, Uppsala, and other mining schools throughout the country, Sweden boasted the brilliant chemists who would unlock these mineralogical mysteries.

For our Rediscovery travels in Sweden, we will first visit Riddarhyttan (pronounced Reed’-ar-huet’-tahn’). The small village of Riddarhyttan is located in the southern part of the Ekomuseum Bergslagen, the original and most important industrial region in Sweden (Figure 1). This “museum” is a scattered collection of about 50 geographical sites that were historically important in the development of the metallurgy of Sweden: copper, silver, but mostly iron, and includes mines, old smelters, waterways, museums, blast furnaces, harbors,

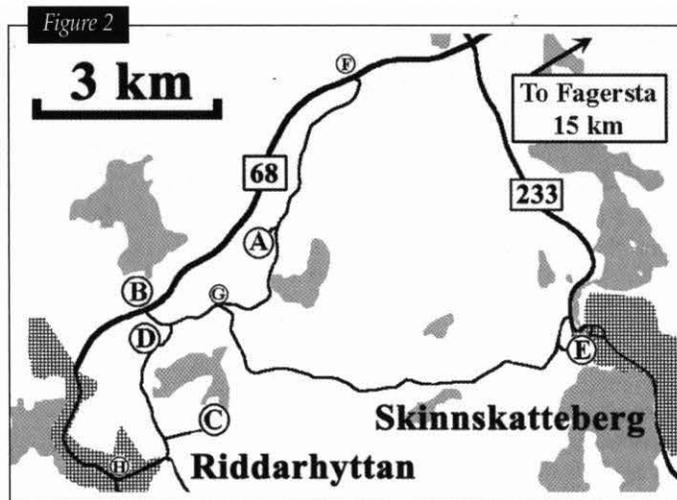


Figure 2. Riddarhyttan holds the following sites of interest: (A) Bastnäs Mine (N59° 50.75, E15° 35.34); (B) old Skilå works (N59° 50.00, E15° 32.99); (C) Kopparverket (new copper works) (N59° 48.89, E15° 34.11); (D) Pellugruvan Mine (N59° 49.64, E15° 33.00) (Brandt old manor foundation is N59° 49.64, E15° 33.16); (E) Hisinger manor on Herrgårdsvagan (N59° 49.71, E15° 40.79). Owing to strict Swedish beautification laws, the number of highway signs is held to an absolute minimum, and few signs exist to guide the tourist. Hence, in order to find these sights it is mandatory to make use of either (1) local bilingual guides or (2) these GPS coordinates. Additional waypoints are given to locate key intersections: (F) intersection main highway 68 with dirt road (N59° 52.06, E15° 36.86); (G) left turn on dirt road to Bastnäs Mine (N59° 50.01, E15° 34.38); (H) intersection in Riddarhyttan to Kopparverket (N59° 48.44, E15° 32.60).

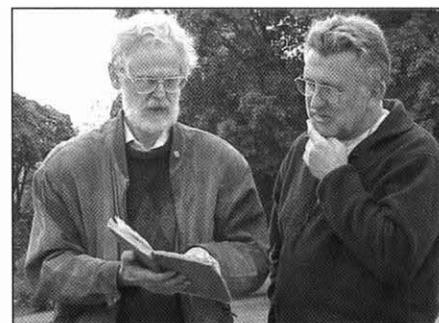


Figure 3. Bengt Hogrelius (left), our guide to the Bastnäs and Hisinger areas, shows one of his prized possessions—an original copy of Cronstedt’s 1758 treatise on mineralogy,³ which originally described the mineral cerite (“heavy stone of Bastnäs”). Cronstedt later called the mineral “falsche Tungstein” after Scheele had discovered the element tungsten (wolfram).



Figure 4. The home of Wilhelm Hisinger, the wealthy mine baron who owned the Bastnäs Mine. This building is currently used as a school for forestry and is maintained in excellent condition. The inside is still furnished with some of the original beautiful woodwork and ornaments, still in pristine condition.



Figure 5. The entrance to the Bastnäs Mine. This mine existed at least since 1692. Mines like this made the iron master Wilhelm Hisinger very wealthy. In the late 1800s tons of cerium ore were extracted, and cerium has been extracted from the slag heaps as late as WWII.

ironworks, canals, etc.³ The Ekomuseum is sponsored by a consortium of local governments and is maintained by over 1500 volunteers, some of whom serve as guides.

Riddarhyttan (Figure 2) is the source of two elemental discoveries—cerium from an iron mine (the Bastnäs Mine) and cobalt from a copper mine (the Pellugruvan Mine). During our visits to Riddarhyttan, we were fortunate to have four Ekomuseum guides, each of whom was experienced in a particular area.

Cerium. Our guide for the story of cerium was Bengt Hogrelus (Figure 3), who first led us to the Hisinger Manor in Skinnskatteberg (Figure 4), seven kilometers to the east (Figure 2). It was at this manor that Wilhelm Hisinger (1766–1852), a wealthy landowner who made his money in the ironworks business, lived and conducted his mineralogical experiments. He had befriended the young, struggling Jakob Berzelius (1779–1848) in Stockholm, who came to visit the Hisinger Manor frequently.⁴ Hisinger showed to Berzelius a strange, heavy mineral procured from this iron mine, and the two curious scientists commenced to study it. This mineral, which they named cerite, was first described by Axel F. Cronstedt (1722–1765, who discovered nickel) in his classic mineralogical reference.⁵

Scheele had previously analyzed the heavy mineral,⁶ hoping to find tungsten (wolfram), which he had originally discovered from a mineral at Bispberg some twenty years previously (1781), but his results were inconclusive. Hisinger and Berzelius thought that the “tung-



Figure 6. Mats Hulander and Ulla Fredriksson guide the authors to the old smelting site (pre-1802) which was used during Brandt’s time. The area is depleted of vegetation, owing to the effects of sulfur dioxide and vitriol produced during the roasting process. Mats is showing how the roasting process is evident by yellow vitriol (iron sulfate) stains on the rocks.

stein of Bastnäs” might contain yttrium, which had been discovered after Scheele’s investigations (Gadolin, in 1794).⁷ But a careful analysis of the mineral by Hisinger and Berzelius revealed no sign of ‘Yttererde’ (yttria). A key distinguishing experiment by the pair of experimenters was an unsuccessful attempt to dissolve their earth in ammonium carbonate solu-

tion;⁸ knowing that yttria was soluble in this medium,⁸ they concluded they had discovered a new earth. They developed a simple procedure to obtain the yellowish cerium oxide (Note 2): dissolve the cerite in nitric acid, neutralize carefully with caustic potash, then add potassium tartrate to precipitate out the pure oxide.⁶ Hisinger and Berzelius published their findings



Figure 7. Reconstruction of the assay house. Inset: an authentic ingot of Kopparverket copper.

in 1804, naming the new earth “cerite”⁶ only to find that Martin Klaproth of Berlin simultaneously had analyzed the same mineral from the very same mine, naming the earth “ochröite” after its yellow color.⁹ Both laboratories produced quantitative analyses showing lime, iron, silice, and over 50% of the new element, consistent with the modern formula¹⁰ of $(Ce, RE)_9CaFeSi_7O_{27}(OH)_4$ [where RE = rare earth].

Whereas Klaproth was content to describe his “ochröite” as merely a new “earth,” the Swedish group appeared to understand more fully the nature of their discovery, which they identified as the oxide of a new metal. They characterized various derivatives (nitrates, tartrates, carbonates, etc.) and the blowpipe properties and even recognized that there may be “different degrees of oxidation.” Even though Klaproth’s paper appeared before that of the Swedish group in *Neues Allgemeines Journal der Chemie* (by one issue), the editor Adolph F. Gehlen favored Berzelius and Hisinger, ostensibly because the Swedish workers more completely understood the nature of their discovery.¹¹ The editor was in the position of being the arbiter of the dispute and decided in favor of the metal rather than the earth; after the famous Parisian chemist N.-L. Vauquelin confirmed the Swedish results, the matter was settled.¹¹ Thus, the element retains the name “cerium” given by Hisinger and Berzelius [after the recently discovered asteroid, Ceres (Note 3)], although both groups are today considered independent co-discoverers. (Note 4)

Bengt next took us to the Bastnäs Mine itself (Figure 5). Iron had been produced in the area for centuries from hematite (iron oxide), which was plentiful about the area. “Usually the ore was taken away in the winter,” explained Bengt, “because sleds on snow were the easiest way to transport it.” Iron forges were common then, and traces of them can be found about the area.¹ Bengt had keys to the locked gate, and we entered the cold, wet gallery. It was no ordinary iron mine inside, because our Geiger counter registered a high count—not an uncommon occurrence in Swedish mines, since secondary minerals leached through Swedish sedimentary layers occasionally include uranium compounds.

Outside the mine, the huge talus piles are still rich in minerals, and several collectors were scrambling about searching for unusual specimens peculiar to this region (cerite, other rare earth minerals, asbestos, etc.). Soon it was time to go, and we were handed a surprise! Bengt gave us a beautiful ruby-colored crystal about the size of a pencil eraser. “Here is a sample of bastnäsite taken from this mine,” he told us. What a treasure! With a formula of $(Ce, RE)CO_3F$, this sample had to be rich in lanthanides. No wonder so many rare earth elements were found in Scandinavia! (Note 5).

Cobalt. Five centuries ago “cobaltum” was described by Agricola;² it was a cobalt-arsenic containing mineral. Cobaltum was well known to Saxony miners because of its poisonous nature and its corrosive effects on unprotected hands and feet. It was easy for the superstitious

miners to attribute these debilitating effects to evil spirits or gnomes in the mines, and the name applied to these minerals was derived from the German word for “gnome” (kobelt).² There was a great deal of confusion about zinc, cobalt, and arsenic compounds at this time, and Agricola lumped them into “cobaltum” and “cadmia” classifications.² Agricola was not able to make the connection between his “cobaltum” and the blue pigment called “Zaffer” used in ceramics (our present-day “cobalt blue”). (Note 6) He could only report that the blue pigment was obtained from the “residues of bismuth ores.”

The person who deciphered the nature of cobalt blue (Swedish “färgkobolt”) was Georg Brandt (1694–1768), Assay Master of the Stockholm Mint. Brandt had been raised at his father’s (Georg Sr.) sumptuous Riddarhyttan Manor (Riddarhyttan Herregård), (Figure 2). Georg Sr. had developed a thriving copper and iron business based on discovering a rich seam of copper ore that played out over a decade as it became mixed with arsenic-containing compounds, including “liusgrå Kies” (“light-colored pyrite”), and which eventually became known as cobaltite ($CoAsS$).¹² Georg Jr., remembering this mineral from his childhood days, collected samples and analyzed them in Stockholm¹² (Note 7). From this mineral sample, Brandt prepared the oxide of cobalt,¹² which he reduced with charcoal using a high temperature furnace to gain a regulus of cobalt.¹³ Further researched showed the new metal was “magnetic” and could be “alloyed with iron.”¹⁴ He showed that the blue color of smalt (the mixture of Zaffer and sand) was due to cobalt and not bismuth, arsenic, or iron as others had incorrectly surmised.¹⁴ Since only a trace amount of cobalt could effect a blue pigmentation, it was now clear that the source of confusion regarding the source of cobalt blue was due to the minute quantity of cobalt in a variety of minerals. (Note 8)

The smelters used for Brandt’s copper ores were located away from the Manor (about half a kilometer to the north), because of the noxious sulfur dioxide fumes produced during roasting. A smelter needed three key ingredients: (1) ore, which could be transported to the site by sled or boat; (2) water for power, and (3) forests to produce charcoal. When a forest was depleted of its wood, the smelter was moved to a new site. In fact, this happened in 1802, when it was moved 2 kilometers south. (Figure 2). Brandt’s industry used the older site.

To help us locate the older site, the director of the Ekomuseum Bergslagen, Mats Hulander (from Smedjebacken, the museum headquarter

ters) and Ulla Fredriksson (a native of Riddarhyttan and a local expert on its history), met us in Riddarhyttan (Figure 6). They described the process centuries ago: a gang of women broke the rocks with hammers; the resulting gravel was roasted on charcoal fires to release sulfur dioxide, and then the roasted ore was heated intensely with charcoal (the smelting process, sometimes repeated several times) to consummate the reduction process and produce elemental copper. The whole process took perhaps two months. The year of the local inhabitants was divided into seasonal activities: summer, plant the crops and harvest; fall, collect wood and prepare charcoal; winter, take ore to the smelting sites; spring, the smelting process is carried out (it was necessary to wait until the ice thawed so that water power would be available for pumps and hammers and washings).

Although the old site is barren of both vegetation and buildings, the new Kopparverket site (Figure 2) has been developed with constructed models of the old pump houses, assay house, and miscellaneous quarters (Figure 7).

To see the Brandt Manor and the mine area, we turned to a couple who live within walking distance of these historic sites. Roy Theiltoft, a retired design engineer who has totally dedicated his time to reclaiming the historic site, and his wife Birgit (Figure 8), have spent several years cleaning up the area, preserving the ecology (once he had to save a drowning moose from one of the flooded mine pits), and setting up signs to guide the visitor. One of his pet projects was to open up one of the ancient mines for visitors. During the dark Scandinavian winters, Roy likes to construct detailed engineering plans of machinery used by the miners. By studying geologic maps and historical records, he has produced accurate and detailed maps of the mining sites about Riddarhyttan.

We spent a whole day with the Theiltofts, roaming about the territory and viewing his intricate computer graphics. To reach the Brandt area, he led us up a winding trail, through the beautiful forests, noting interesting features along the way. "There's an old claim," he pointed; "the miners used to make their claim by piling up rocks." Then he led us to the Manor area, which now consisted only of the original stone foundation and a few minor stone shacks. Finally, he took us through a dense grove to the mines themselves, 100 meters further west. "There is a series of mines, Hedringegravan, Pellugruvan, Kanthalgruvan, Sögruvan, and so on, each only fifty meters or

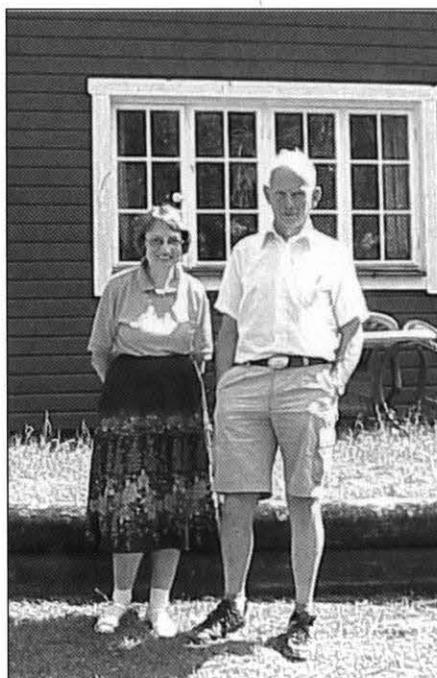


Figure 8. Roy and Birgit Theiltoft live at "Rödgruvan" ("red mines") named after the ancient copper mines which predated even the Brandt mines. A ten-minute walk from their charming home allows one to visit the historic Brandt area.

so from the next." But the mine that was of major interest to us was Pellegruvan, (Figure 9) because of the beautiful specimens of cobaltite (CoAsS) which have been found there. It is very likely that this was the very mine that furnished the cobaltite¹² for Brandt's discovery. (Note 9) Roy then issued us hardhats out of his knapsack and led us inside his pet mine. "Look on the floor," he directed our attention to hollowed-out logs, "they used wooden pipes to pump out the water." Inside, we saw beautiful red and blue-green crystals growing on the sides on the wall, attesting to the rich mineral content of the hillside.

When Roy works on his computer, he spends most of his time detailing the engineering - the crushers, the bellows, the lifts, the tools, the carts - used by the men of that historic time to extract the ore, to crush it, and to smelt it, as well as 3-dimensional maps of mines detailing the intricate shafts and galleries. But he has also turned his attention to produce a design to capture the spirit of Riddarhyttan (see Figure 10). This motif adorns the welcoming pamphlet to the Riddarhyttan community society ("Riddarhyttans Hembygds- och Intresseförening"), with which

he and Birgit are so actively involved and which promotes community interest in the local ecology and history. Indeed, the world community itself is very fortunate to have hundreds of dedicated volunteers like Roy and Birgit, as well as Mats, Bengt, and Ulla, to preserve the scientific and cultural heritage of so beautiful a country. ☺

Acknowledgments.

The authors are indebted to Bengt Hogrelius, Mats Hulander, Ulla Fredriksson, and Roy and Birgit Theiltoft, for their gracious assistance in locating the sites of interest in Riddarhyttan and in providing a wealth of information about its history. The authors also are grateful to Per Enghag, the author of Ref 12 and a expert in the Swedish history of the elements, for providing detailed information on the research of Brandt as well as the location of Laboratorium Chymicum in Stockholm.

Notes.

Note 1. If one tabulates the source of the ore of elements (metals and semimetals) discovered in the past 500 years, one finds: Sweden, 10 (Co, Ni, Mn, W, Ta, Sc, Mo, Li, Y, Cc); Germany, 7 (Ge, U, Cd, In, Th, Cs, Rb); Norway, 2 (Th, Hf); Russia, 2 (Cr, Be); Czech Republic (Bohemia), 2 (Ra, Po); Brazil, 1 (Pd); Colombia, 1 (Pt); England, 1 (Ti); France, 1 (Ga); India, 1 (Zr); Mexico, 1 (V); Romania, 1 (Te); Scotland, 1 (Sr); United States, 1 (niobium). This list does not include: (a) elements whose source is multifold or ambiguous and which were discovered as impurities in previously discovered elements, viz., the rare earths, the platinum metals (most of which were isolated from South American material), and the trace radioactive elements; (b) elements surmised as such by Lavoisier, whose parent substance had been known for centuries, viz., Al, Si, B, Mg, Ca, Ba.

Note 2. Little did Hisinger, Berzelius, and Klaproth know that the "yellow" cerium oxide (which actually is white when pure) harbored many new "rare earths." After over 100 years of tedious research, investigators separated the "light rare earths" from cerium (with a larger atomic nucleus, in the first half of the lanthanide series)—while analogous research gave the "heavy rare earths" from yttrium (with a smaller atomic nucleus resulting from the lanthanide contraction, in the second half of the lanthanide series).

Note 3. Ceres, the first asteroid, was discovered on 1 January 1801 by Giuseppe Piazzi, at the Royal Observatory (N 38° 06.69, E 13° 21.17) at the Norman castle (Palazzo dei Normanni) in



Figure 9. Pellegruvan, the copper mine which most likely furnished the ore analyzed by Brandt in his discovery of cobalt. The mine is now flooded with water and resembles an old swimming hole.

Palermo, Sicily, the same city in which the element technetium was discovered in 1937.

Note 4. We will withhold full stories of these famous chemists, Berzelius and Klaproth, until a future time. For a complete treatment of Berzelius, we are awaiting the finalization of the Berzelius Museum, previously at the Swedish Academy, but which materials are now in storage (including original samples of cerium oxide) and awaiting installation at the Observatory Museum in Stockholm in a few years.

Note 5. Upon arriving home, we had it analyzed by EDX (energy dispersive X-ray) and found the impressively high percentage values of 29% Ce, 26% La, and 6% Nd, with trace amounts of other rare earths. (A photograph of this sample is displayed in *Walking Tour of the Elements*, CD-ROM, 2002, produced by the authors). Bastnäsite is found in many sites throughout the world, but rarely so beautiful as specimens from the Bastnäs Mine.

Note 6. Bernard Palissy (1509/10–1589/90), a Parisian glassmaker and ceramist, was familiar with Zaffer (ref 14, Partington, vol 2, p 69–77). Some of his ceramics may be viewed in the Musée de ceramique (Ceramics Museum) of

Sèvres, western outskirts of Paris; his statue stands in front of the museum (N 48° 49.73; E 02° 13.40). Both “zaffer” and “smalt” were terms used for blue coloring/sand recipes used in the ceramics trade.

Note 7. Under Georg Brandt’s leadership, the Laboratorium Chymicum became a very important institution in Europe. The Laboratorium Chymicum was set up by the Royal Board of Mining and Metallurgy (Bergskollegium) in 1630 under King Gustavus II Adolphus and over the years was located at various sites. At the time of Brandt, it was situated at the approximate site of the present Serafimer Hospital (N 59° 19.71; E 18° 03.19), across the street (Hantverkargatan) from the City Hall on Kungsholmen. Georg Jr. was less interested than his father in the economics of a copper business but more in the chemical classification of metals and ores, and he traveled frequently between Riddarhyttan and Stockholm.

Note 8. There is a great deal of conflicting information regarding just when, and how, G. Brandt discovered cobalt, as is clear from Partington’s analysis (ref 14, Partington, vol. 3, p 168). P. Enghag, an expert in Swedish chemical

history, relates “There has been some confusion about the discovery year for cobalt. As Brandt himself says, he gave this information to the Academy in 1735, and this year is often considered the discovery year for cobalt. My original information [published in ref 12] had Brandt in 1730 using CoAsS (cobaltite) from Riddarhyttan. But Professor Torbern Bergman [in Uppsala] said in his commemorative speech in 1769 that Brandt had investigated the ‘blue glass Safflor’ and had found the element cobalt there. In 1748 Brandt published results of further investigations of the new element. As raw material this time he used the mineral linnæite Co_3S_4 from the mine of his childhood in Riddarhyttan [near Bastnäs]. He succeeded in preparing a regulus of the metal and he reported of its magnetic properties.” [P. Enghag, personal communication]. Much of the mystery lies in the obscurity of the original Swedish publications. Translations of these original papers appear in *Recueil des Mémoires les plus Intéressants de Chymie, et d’Histoire Naturelle, contenus dans les Actes de l’Académie d’Upsal, et dans les Mémoires de l’Académie Royale des Sciences de Stockholm, 1720-1760, P. fr. D. LeJeune, Paris, 1764*, where the pertinent papers of Brandt appear: “Dissertation sur les demi-métaux” [which includes mercury, antimony, bismuth, cobalt, arsenic, and zinc], Vol. 1, pp. 8–25 (1735); “Examen d’une nouvelle espèce de cobalt” [which is now known as linnæite, Co_3S_4], Vol. 1, pp 38–50 (1742). From all information it appears that Brandt realized his discovery gradually over the period 1730–1745 from a manifold of simultaneous approaches, including analysis of cobaltite (CoAsS) from his father’s estate in Riddarhyttan, reduction of färgkobolt from various sources, and later reduction of arsenic-free cobalt sulfides from the Bastnäs Mine in Riddarhyttan.

Note 9. A photograph of a sample of cobaltite from Pellegruvan is displayed in *Walking Tour of the Elements*, CD-ROM, 2002, J. L. and V. R. Marshall).

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Figure 10. There are many villages in Bergslagen with the "hyttan" suffix which means "smelter" or "blast furnace." "Riddar" means "knight." This motif, designed by Roy Theiltoft, symbolizes the spirit of Riddarhyttan.

