Verneuil's Rubies
Auguste Verneuil (1856 – 1913)

Where should we go for a field trip? When a colleague suggested the Minerals Gallery at the Natural History Museum it seemed a no-brainer; the range of materials and crystals would suffice to inspire the most jaded of scientists. And as we wandered through the gallery, stories billowed about chemistry and how we've learned about our world. With one group of students I paused by a case of synthetic crystals marvelling at a rod, opaque at one end, before narrowing down to a narrow neck and then swelling to a stunning deep red ball of ruby. "Grown by the Verneuil process", read the label. I told my students I had no idea, and promised that I would find out.
Attempts to make gems disappear into the mists of time, but only became serious in 19th century as chemical analysis gradually revealed the peculiarities of different gemstones. While diamond was shown by Smithson Tennant to be composed of pure carbon, others found that rubies and sapphires were made mostly of alumina with small amounts of metals; there also seemed to be silicon but in small, variable quantities. It was not until the 1830 that Heinrich Rose, the German codifier of qualitative inorganic analysis and reigning master analyst, proved that the silicon was a contaminant introduced when the stones were ground in an agate mortar. Thus the problem of making gems was reduced (to misrepresent the challenge) to find a way to melt and crystallise highly pure alumina. This material was available thanks to the work of Gay-Lussac who had shown that thermal decomposition of ammonium alum gave exceptionally pure aluminium oxide. Its availability would lead Ste. Clair de Ville and Robert Bunsen to explore its electrolysis to smelt the metal, using a variety of double salts as fluxes. A sample of the French chemist's original aluminium is currently on display at the London Science Museum in Louis Napoleon's collection of elements.
But the problem of melting crystallizing molten alumina remained. Marc-Antoine Gaudin (1804-1880) was one of the first to obtain tiny crystals of corundum, thin, clear platelets generated in the flame of a gas and air torch. Adding a little chromium into the mix, he obtained tiny deep red rocks which were infuriatingly opaque due to the presence of gas bubbles trapped in the crystal. Try as he might Gaudin was unable to obtain anything clear – the crystals "devitrified" (became opaque) every time. After 30 years of experiments his final, crushed conclusion was that he had reached a dead end. He died soon after.
Meanwhile at the the Jardin des Plantes, the natural history museum in Paris, the chemist Edmond Frémy chose a more conventional approach. With help from the glassmaking firm St Gobain, Frémy and his assistants heated huge platinum crucibles containing tens of kilogrammes of alumina and various salts hoping to obtain quality gems. Yet even after 10 days in the furnace all they obtained were minuscule crystals. In the 1870s Frémy was joined by an assistant C. Feil and by a young apprentice Auguste Verneuil, only 17 at the time. Verneuil, whose father had moved into photography, had developed a passion for chemistry as a teenager; he managed to secure a place in Frémy's lab, an association that would continue until his mentor's death.
Platinum being too expensive, they developed a method using sand crucibles, in which careful filling with a mixture of alumina, potassium carbonate, chromium oxide and charcoal surrounding a core of alumina and calcium fluoride resulted in the formation of thin but millimetre-long clear crystals. Crucially the decomposition of the carbonate produced bubbles in the melt that allowed moisture to penetrate generating traces of hydrofluoric acid – the resulting volatile aluminium fluoride was essential to the crystal growth. Feil died suddenly in 1876 and Verneuil succeeded him as the Professor's assistant. This gave him a lab of his own where he could his own experiments. Verneuil lost no time in getting formal qualifications.
In his book on the preparation of rubies Frémy paid tribute to both Feil and to Verneuil referring to the latter as "a young researcher filled with *ardeur* (enthusiasm) and talent", adding that any supervisor would be "pretty thrilled to find a co-worker such as Monsieur Verneuil".
When Frémy retired in 1892, Verneuil became Professor of Applied Chemistry. He now had the freedom to choose his own projects. Their range was astonishing. There were 16 papers on the rare

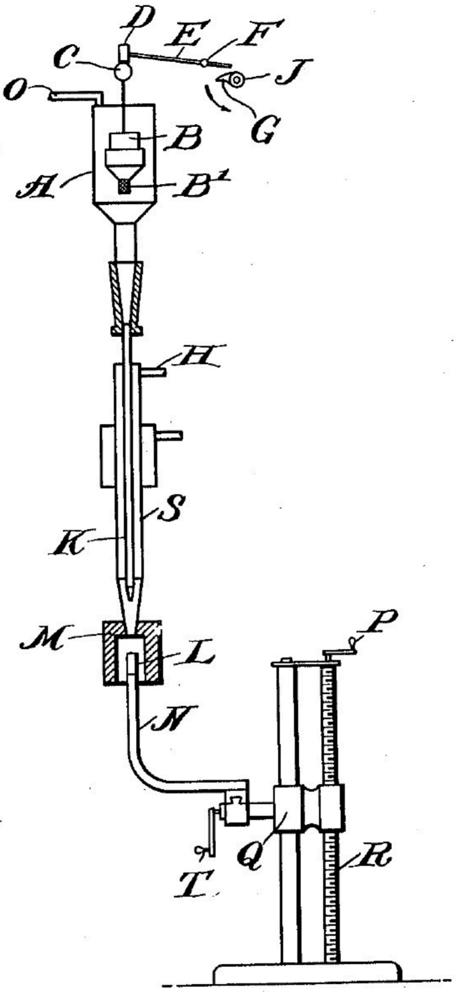
earths, multiple studies of the chemistry of selenium, investigations of the phosphorescence of zinc blende. He also also advised a glycerine manufacturer. There was the lecturing. had his own brilliant experimental assistant Marc Pacquier.

The appearance of some small but clearly synthetic rubies in a saleroom in Geneva in 1885 was a wake up call. A colleague of of Verneuil's PME Jannetaz examined them showing that whoever had made them had taken natural rubies and succeeded in melting them into a single, clear gem. Verneuil went back to Gaudin's ideas of heating alumina in flame, but trying Ste. Clair de Ville's hotter oxy-hydrogen flame. In Verneuil's method aluminium oxide was dropped from a hopper into a hot zone where it was melted into droplets. These landed on a support that was gradually lowered as the crystal grew. The hopper was tapped periodically to get slugs of powder to rain into the flame. Layer by layer a *boule* would grow, initially spherical but then more elongated. After a couple of hours the flames would be switched off leaving a transparent crystal. The only problem were the internal stresses which required the crystal to be split down the middle by tapping gently with a hammer. Although the layers could be seen under the microscope, along with minute bubbles aligned perpendicular to the layers, the quality was astounding and lapidaries were happy to cut the stones into gems. Verneuil and Pacquier were careful to submit a sealed note of their invention to the Academy of Sciences in 1886 and then optimised the method before making a public announcement in 1902. Verneuil and Pacquier would go on to make blue sapphires which they described carefully in their patents along with their characteristics, lines, cracks and bubbles. Today, leaving aside the ultra-hard corundum of our sandpaper, synthetic rubies and sapphires are everywhere, often made by this very process, from our watches to specialist unbreakable windows and tubes for extreme experiments. Perhaps it is the ultimate testament to the tenacity of Auguste Verneuil that he is almost forgotten, and his materials taken for granted.

Reference

A. Verneuil, " Memoire sur la Reproduction du Rubis par Fusion," *Ann. Chim. Phys . Ser* 8, **1904**, *3*, 20-48.

Fig. 1.



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