Article:

Hammond, C, Edyvean, R and Yardley, B (2018) The Chemical Precipitates of Henry Sorby. Elements, 14 (3). pp. 214-215. ISSN 1811-5209

https://doi.org/10.2138/gselements.14.3.214

The Chemical Precipitates of H.C. Sorby: early experiments on mineral morphology

Chris Hammond[1], Robert Edyvean[2] and Bruce Yardley[1]
[1]University of Leeds, Leeds LS2 9JT, UK
Email: C.Hammond@leeds.ac.uk, B.W.D.Yardley@leeds.ac.uk
[2]University of Sheffield, Sheffield S1 3JD, UK
Email: r.edyvean@sheffield.ac.uk

Henry Clifton Sorby (1826-1908) is best known to geologists for pioneering the use of the petrological microscope and instigating the systematic study of fluid inclusions, but he also introduced microscopy to many other areas of science. He belongs to that great tradition of amateurs which has made substantial contributions to science. Being unhindered by the needs of funding bodies, Sorby's research ranged very widely and touched on many topics that are still current today.

In 1879, Sorby published a short paper in the Mineralogical Magazine "On the cause of the production of different secondary forms of minerals". He begins "It has often struck me that much more might be learned from the study of the secondary forms of crystalline minerals than we now know respecting the circumstances under which they were produced. Some years ago being chiefly acquainted with calcite as it occurs in Derbyshire, where the crystals are usually of the so-called dog-tooth shape, my attention was much attracted by the difference in the form of crystals in Devonshire and Cornwall, where we so often meet with six-sided prisms… I could not give any more satisfactory explanation than that the conditions under which they were formed must have been very different in some important particular.'"

Sorby goes on to describe a series of experiments in which he prepared aqueous solutions of 'carbonate of lime in carbonic acid', then evaporated them at different temperatures. He reported that differences in temperature, the presence of "foreign substances" (Fe and Mg carbonate were sometimes added) and conditions of formation (including whether crystals formed at the surface or the bottom of the solution) gave "rise to very varying forms of the crystals… but I did not continue the experiments sufficiently to enable me to draw upon any complete detailed conclusions." He concludes "If this could be done, it would, I doubt not, be a great gain for geology".

It appears that Sorby then abandoned this avenue of research, but he was always meticulous in preserving his microscopical preparations – sometimes publishing his results long after completion of the experimental work. For example, all his work on the microstructures of iron and steel, were carried out in 1863-65, but remained unpublished until 1886-7. But the preparations of the crystallisation experiments, upon which the 1879 paper is based, have never come to light until 2011 when one of us (RE) discovered, at the back of a store cupboard in the Department of Chemical Engineering, University of Sheffield, a blue-paper covered cardboard box labelled 'Chemical Precipitates *&c'*.

The box and its contents are shown in Fig. 1. It contains sixty 40 mm square glass slides (with coverslips) all neatly diamond-point engraved with brief descriptions and the initials 'H.C.S.' and date (Fig. 2). Without doubt, these are the long-lost preparations. Most are conventional microscope slides and it appears that crystalline precipitates from the experiments were collected onto the slides and preserved with a coverslip. These are in immaculate condition with little yellowing of the Canada balsam, and no detachment. Most of these slides are dated 1852, with a few from later years up to 1862. There are also ten cavity slides (i.e. with a shallow well), all but one (undated) from 1858. The exact nature of the cavity slide experiments is unclear (see description for Fig. 2B). Most of the chemical precipitate slides precede the year (1855) in which Sorby commenced his research on fluid inclusions but the description on the later cavity slides may indicate that they were used for evaporating the leachates from crushed fluid inclusion-bearing minerals.

The engraved notes on the slides are the only source of information about the experiments that generated these products, so we have a tantalising glimpse into the controls on crystallisation that Sorby investigated, without being able to reach any definite conclusions. The notes show that Sorby carried out a greater variety of experiments than described in his brief paper of 1879. As well as evaporating solutions of carbonates he also added sodium carbonate to calcium chloride or the reverse.

We have re-examined the slides using optical microscopy, but have not attempted to use any destructive techniques. There appear to be three main types of solid product, sometimes present together (Fig. 3). Many slides contain well-formed single crystals up to 20 μm across and with a rhomb-like morphology and high birefringence (Fig. 3A). In others, the precipitates are in the form of spherulites of highly birefringent radiating fibres with straight extinction (Fig. 3B). Often spherulites form “dumbbell shapes”, rather than simple spheres. A few experiments produced acicular crystals, and these invariably coexist with rhombs. (Fig. 3D, E). Both the fibres in the spherulites and the acicular carbonate crystals have straight extinction, and are inferred to be aragonite, while the rhomb morphology is inferred to be calcite. Without knowing the starting compositions, we cannot be sure if other divalent carbonates may have precipitated, but slides from experiments with Fe-carbonate do show slight orange discolouration.

The experiments which only produced rhombs involved evaporation of calcium bicarbonate solutions, generally under mild conditions. In contrast, the precipitates in samples formed from mixing calcium chloride and sodium bicarbonate solutions are spherulites of highly birefringent radiating needles with straight extinction (Fig. 3B). Some experiments produced a mixture of spherulites and rhombs (Fig. 3C), and these are described as deriving from evaporation of carbonate solutions under relatively extreme conditions, including boiling and addition of MgO and FeO. The experiments which produced distinct acicular crystals coexisting with rhombs. (Fig. 3D) also involved relatively intense evaporation, and include one experiment in which cotton was provided for the precipitates to grow on (Fig. 3E).

Sorby noted that crystal morphology sometimes varied according to whether they formed at the surface or the base of the evaporating solution, but did not provide more details. Some of the slides with mixed morphologies may reflect this phenomenon. In present day terms, we can infer that spherulitic morphologies are indicative of growth from supersaturated solutions, while single rhombs would suggest a lesser degree of supersaturation.

What do we learn from Sorby’s experiments, and are they relevant today? The short answer is that Sorby failed to find answers to the questions he set out to tackle, and with the benefit of hindsight it is not difficult to see why. He had no means of identifying his precipitates beyond the microscope and it would be well into the twentieth century before crystal growth theory was able to provide an adequate framework for his observations. However what is clear from his 1879 note is that he had realised that crystallisation can be very strongly dependent on subtle factors which may not appear to be at all significant at the outset. It was lessons like this which led to modern ideas of “good scientific practice” where parameters are controlled to the point where experiments become reproducible. Sorby’s slides gives us an intimate glimpse back into the early years of modern science, with a chance to see how an individual scientist was thinking and modifying his ideas while coming to terms with unexpected difficulties in the work. His experiments were a failure in their original terms, but not a waste, and he bounced back from the frustration to embark on the study of fluid inclusions where he had a lasting impact.

Further Reading

Sorby HC (1879) On the cause of the production of different secondary forms of minerals. Mineralogical Magazine 3: 111-113

Edyvean RGJ, Hammond C, (2017) Henry Clifton Sorby's pioneering work on the metallography of iron and steel. Sorby Record No.53 (in press)

Higham N (1963) A very scientific gentleman – The major scientific achievements of Henry Clifton Sorby. Pergamon Press, Oxford, 160pp.

Figure Captions

Figure 1 Sorby's original cardboard slide box, 165 mm square by 48 mm deep with three rows of edge-mounted slides. We have numbered the slides according to their order in the box rather than by their date or content.

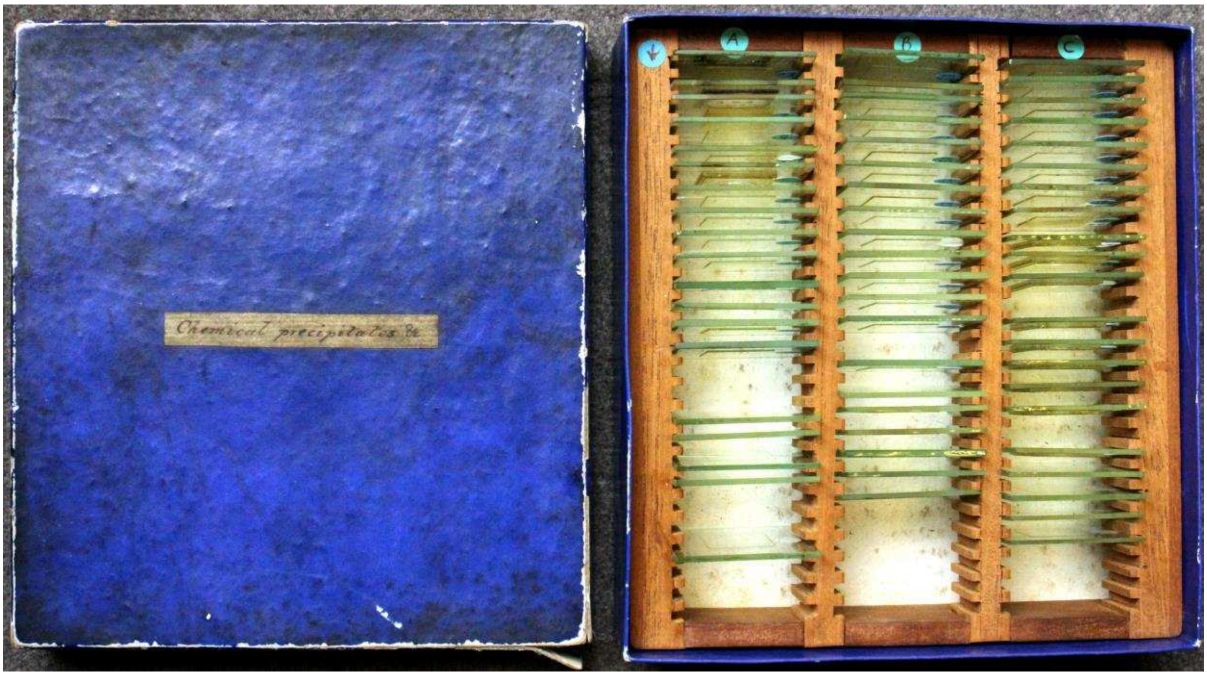


Figure 2 Examples of Sorby's chemical precipitate preparations. Each slide is 40 mm square. (A) Slide 4, a standard side inscribed 'CaO.2CO_2 evap at about 70ºF H.C.S. 1852'.

This slide exhibits well-developed rhombohedral crystals (see Fig. 3A). (B) Slide 52, cavity slide inscribed ‘salts sol in water in quartz of granite C. Cornwall. H.C.S. 1858’. Perhaps this slide contains the remains of an early attempt to investigate fluid inclusions by crushing. Note the deterioration (yellowing) of the Canada balsam in the cavity slide.

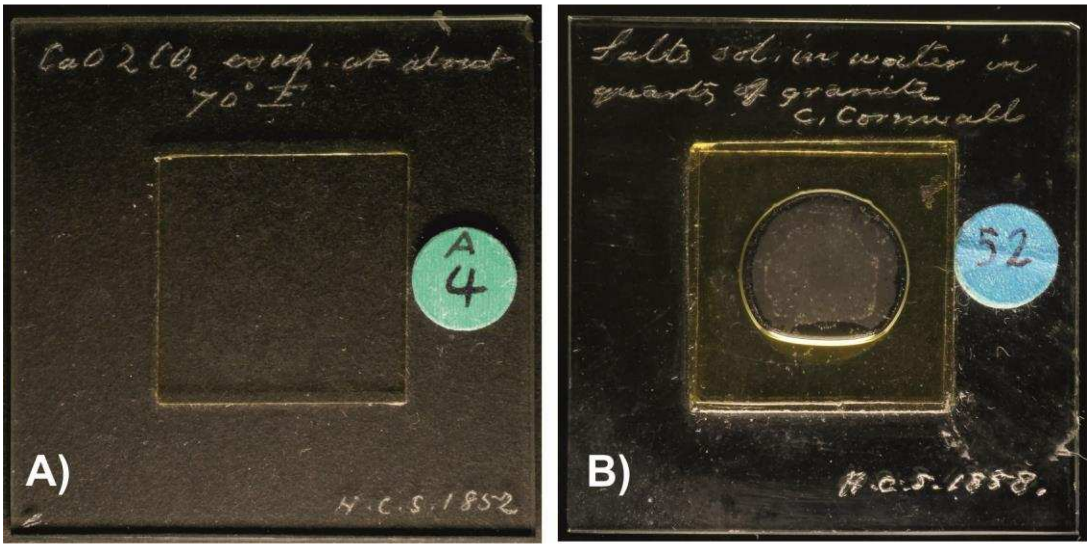
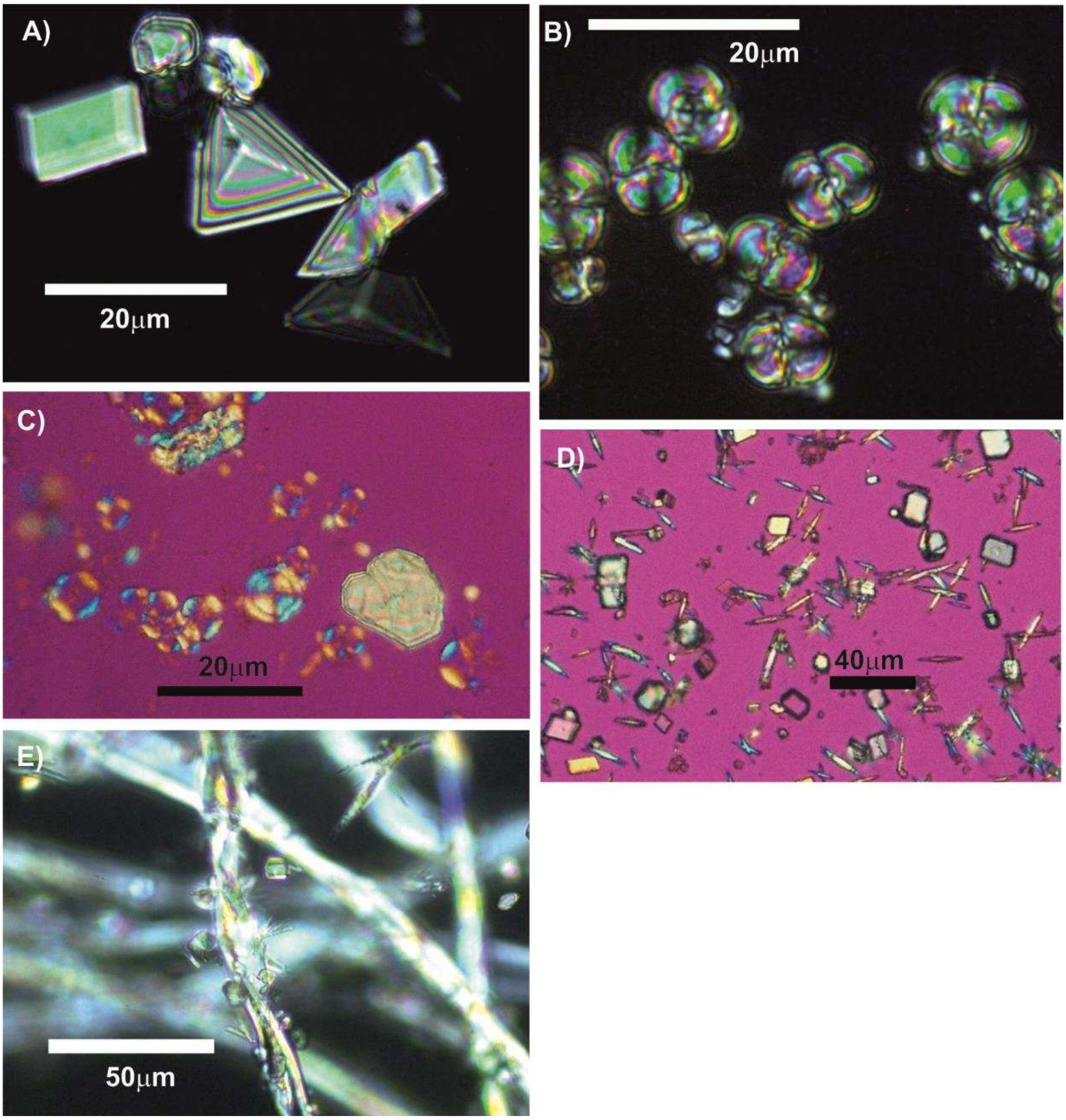


Figure 3 Photomicrographs of precipitates from Sorby’s experiments, all with crossed polars. (A) Slide 4 (see Fig. 2A), example of coarse rhombohedral crystals, inferred to be calcite. (B) Slide 21, inscribed ‘CaCl in ex^{s} added to carb am$^{\alpha}$ $^{x}Fe_2O_3$ present H.C.S. 1852’, examples of spherulites made up of fine needles with straight extinction. (C) Slide 35, inscribed ‘Bicarb. CaO.MgO FeO evap. at 80^{o}F H.C.S. 1852’, spherulite textures are represented by very thin, radial growths of fine needles and coexist with much thicker rhombs. (D) Slide 2, inscribed ‘$CaCO_3$ cryst on glass from CaO & CO_2 (indecipherable) H.C.S. 1852’, acicular crystals, commonly twinned, coexisting with rhombs. (E) Slide 3, inscribed ‘CaO.2CO2 evap. at max. heat & crys^{t} on cotton H.C.S. 1852’, both acicular crystals and rhombs occur adhering to the cotton threads.


A)
20μm
B)
20μm
C)
20μm
D)
40μm
E)
50μm