## WHEN ACCESSORIES ARE ESSENTIALS



Bruce Yardley

In the early days of its development, the petrological microscope's value was far from universally accepted. Pioneers like H. C. Sorby were ridiculed by those who believed that it was impossible to learn anything about mountains by looking down a microscope. Changing scale in this way comes naturally to most Earth scientists today; we have learnt to value the subtle as well as the big and obvious. This *Elements* issue is dedicated to just one mineral, tourmaline, which is almost never in the vanguard of rock-forming minerals but is remarkably common in the background as an accessory

phase. One of the most endearing and useful features of tourmaline to me is that it is usually very easy to recognise in hand specimen and under the microscope. This matters because showing tourmaline to a student in a rock or a thin section provides both a boost to their confidence – it is a relatively unusual mineral that should be easy to recognise again – and an opportunity to show that a fascinating range of aspects of geology can be explored just because tourmaline is there. Students often see the major divisions of the Earth sciences as entirely separate topics, delivered by different professors, carried around in different parts of the brain and brought up in different exams. A discussion about how tourmaline in a schist might mean that the parent sediment was marine or how the triangular coordination of boron may be reflected in the mineral's morphology may prod them towards that visionary moment when they suddenly realise that all sorts of different stuff actually fit together. Set against that of course is the painful memory of those intransigent black residues at the bottom of the crucibles when I tried to do wet chemical analyses of tourmaline-bearing rocks!

Like many other accessory minerals, tourmaline is generally left out of consideration when we investigate how the rocks that host it have formed. Our understanding of granites and granitic melts is based mainly on experimental investigations of combinations of quartz, feldspars and perhaps micas, but only pegmatite enthusiasts have considered the effects of the components present in accessory minerals. That was a reasonable starting point when we had no idea about the actual melting points of magmas, but of course where tourmaline is present, there must be boron, and boron is an effective flux.

When rigorous and quantitative experimental petrology blossomed half a century ago, it was obviously more useful to study simple endmember systems from which thermodynamic data could be extracted and applied to a range of natural systems, than to investigate the infinite range of natural systems. The drawback is that minor components which may have an important influence, whether on melting temperatures, solubilities or even conditions of equilibrium between phases, get left out. Fortunately, these are often components, like B, which do not vary randomly in nature but are buffered by the presence of the accessory minerals in which they predominantly reside. Accessory minerals allow us to investigate more complex, and hence more natural, systems in a very measured and controlled way – the number of components increases, but the degrees of freedom do not.

The effects of additional components are particularly marked when it comes to mineral (or rather, rock) solubility. Based on the low solubility of corundum in water, we thought for many years that Al is an element with extremely low solubility in the crust. There is not a geochemical modelling code in existence that will not tell you the same thing. Only very recently have the innovative experiments of Craig Manning and Bob Newton established that although corundum is very insoluble on its own, if you put an Al-silicate with other minerals, Al will form complexes with Si and Na in solution so that its solubility goes up significantly. Thank goodness for that, because how else could those beautiful Al-bearing minerals be forming in hydrothermal veins? And of course, one of the most widespread Al-rich vein minerals is tourmaline, so is it just possible that B also plays a role in enhancing Al solubility?

It is not my place to pre-empt the editors and authors of this issue in extolling the virtues of tourmaline, but it really is a very valuable marker for understanding the environment in which it grew, even if all the possible constraints have not yet been calibrated. Not only is it stable over a wide range of pH and redox conditions, but there are lattice substitutions that will reflect these variables. That is quite a combination – for example, for understanding late-magmatic volatiles – and it has the potential to address issues which would otherwise be completely intractable.

Of course tourmaline is just the latest of a number of accessory minerals to have come in from the cold and be recognised for their contributions to the larger science. The arrival of the microprobe meant that petrologists began to take opaque minerals seriously, instead of referring to them as "ores" (thereby displaying as little knowledge of economics as of reflected-light microscopy). The minerals that can be dated were next to reach prominence. If we understand where they form in the petrogenetic history and can obtain an age for them, minerals such as zircon and monazite take on a front-line role in unravelling the history of metamorphic belts. Apatite also is proving to be another valuable monitor of the behaviour of some of those minor components that are so hard to nail down but can have a profound influence on how a geochemical system behaves.

The Earth sciences, probably more than any others, have advanced by guesswork. Not just any guesswork, but good guesswork founded on observation and an understanding of underlying scientific principles. It made sense to start investigating how rocks form in the deep Earth by looking at simple systems of wide applicability, but having done that, it was inevitable that we would start speculating about all sorts of details of deep-Earth processes. Studies of accessory minerals provide new constraints and tests for those speculations, and we can now move on to a higher level of guessing.

Most of the time, the things that we learn from accessory minerals and the other minutiae beloved of the careful petrographer provide a refinement of our ideas but don't completely overturn them. Just occasionally, however, the minutiae turn out to profoundly change our understanding. The recognition of coesite and diamonds in eclogites has transformed high-pressure petrology and has led to completely new models for the tectonic settings from which eclogites may be derived and the means by which they return to the surface. At an even smaller scale, halite daughter crystals in fluid inclusions have revealed that chloride salts play a fundamental role in fluids from the mantle to the surface, transforming ideas about metal solubility and transport and requiring the development of two-phase flow models to properly address deep fluid flow. Not bad for a mineral that rarely exceeds a few micrometres across in high-T rocks, and a great vindication of the faith of H. C. Sorby in the value of thin sections; it was he who first noticed halite in fluid inclusions, in a granite from Aberdeenshire.

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