Question: Unusual Pocket Find

The photo shows an unusual mineral association from a pocket in a Southern California Pegmatite. In the background is a rehealed base (now doubly terminated) of quartz crystals from which a highly corroded schorl extends out about 4 cm. Within it's hollowed out core are perched a number of orange red sphene crystals from 2mm to 5mm (see Photo 1).

I have a number of questions concerning the changes in pocket chemistry that would lead to corrosion of some minerals within pockets such as schorl or beryl in one portion of the pegmatite while in other areas of the same pegmatite beryl or schorl will show little or no corrosion, so if you have anything I could read to help me in this area it would be greatly appreciated. Such zones of corrosion appear to be highly mappable and specific to individual minerals such as schorl, beryl, topaz, or herderite within the same dike. I am trying to see if an understanding of corrosion effects in the pegmatites I'm exploring can lead to better decisions on directions of future exploration.

Sincerely, Nicholas J. Rose

Responses: Etching, Selective Dissolution, and Hollow Growth

In reply to the question posed by Nicholas Rose, here are three responses to date:

From Prof. Robert F. Martin, McGill University:
“Hollow tourmaline need not have an origin by etching or by corrosion. Crystals that grow at high supersaturations may well grow as hollow prisms. I would suggest to Mr. Rose to consult *The Canadian Mineralogist*, volume 16, page 288, Figure 11. The synthetic crystals of chlorapatite look like hexagonal drinking straws. Hollow crystals result from growth, not dissolution or etching.”

From Dr. John S. White, Kustos
“Even though I have written a short piece for *Rocks & Minerals* ("Disbelieving Dissolution" Nov/Dec 2002) in an attempt to refute the claim that tourmaline scepters are the result of etching, I hardly consider myself an expert on the subject. Just the same, the image that accompanied the Nicholas Rose query doesn't give one much to work with. In that particular instance I would be reluctant to assume that the hollow schorl was produced by dissolution of schorl at its center. Rather I would lean toward interrupted growth or the schorl having grown around a crystal of something else that has been etched away.

I am reminded of an article that appeared some thirty or more years ago in Am. Min. (I believe) about quartz infilling hollow tourmaline crystals. I was troubled that the author offered no proof of interpretation and did not appear to consider the possibility that the quartz crystallized first and tourmaline then grew around it.”

From David London
Drs. Martin and White have pointed out three possibilities for the hollow tourmaline crystal shown by Mr. Rose:

- growth of a hollow crystal from an aqueous (or other solvent) medium, leaving the center open when that fluid medium is no longer present (Prof. Martin’s suggestion);
- growth of a (hollow) tourmaline crystal along with or around a crystal of another mineral, with subsequent selective dissolution of the central crystal (Dr. White’s suggestion); and
- selective dissolution of the core of an originally complete tourmaline crystal (noted by Dr. White, but not his preferred explanation).

The tendency for crystals to grow rapidly on corners and edges, which follows from Pauling’s rules for crystal growth, produces skeletal or hopper crystals in which faces have failed to advance at the same rate as corners and edges. As Prof. Martin notes, this growth habit normally results when crystallization commences from a highly supersaturated solution, and it also reflects a condition in which the growing crystal initially is far from chemical equilibrium with its nutrient solution (aqueous or magmatic). Morgan and London (1988) observed that when the driving force to precipitate tourmaline from an aqueous solution increased, the habit evolved from fully formed euhedral crystals to columnar or fibrous growth pillars in the [0001] direction of the crystal. This skeletal growth habit generates fibrous or bundled/compound single crystals of tourmaline, which are common in pegmatites, and it is also the source of the cat’s-eye effect in tourmaline. The habit is different, however, from the hollow crystal shown by Mr. Rose.

The second case begins as an extension of the first, except that the core of the hollow tourmaline crystal is filled with one or more minerals rather than an aqueous fluid phase. Hollow crystals of black tourmaline and beryl (filled with quartz, albite, etc) are common, as are skeletal crystals of phosphates intergrown with albite. All are analogous to graphic granite – the skeletal intergrowth of microcline and quartz (see Fenn, 1986) – and all originate from the same process, in which crystals begin to grow from a medium (pegmatite-forming silicate melt in this case) that has become highly supersaturated in mineral components. Dr. White suggests that subsequent and selective dissolution might have removed the core-filling material but not the surrounding tourmaline in Mr. Rose's. Selective dissolution of certain minerals is widespread in pegmatites and may result in pseudomorphism (Fig. 1) or complete removal (Fig. 2), while surrounding minerals remain unscathed.

The third case mentioned by Dr. White also entails selective dissolution, but in this case tourmaline also constitutes the core of the crystal. Compositional zoning parallel to the [0001] growth direction is common enough in tourmaline, but the question is: how different must the core composition be to dissolve completely while the rim remains essentially intact? Is this feasible?

I concur completely with Prof. Martin and Dr. White that the processes they describe (skeletal growth, selective dissolution) are important phenomena in pegmatites. In the particular case of Mr. Rose's tourmaline, however, I have some samples – also from pegmatites in southern California – that appear to support an origin for these hollow crystals by selective dissolution of interior zones of tourmaline.

Figure 3 shows a suite of tourmaline crystals (5 of 16 such pieces) from an extension of the Topaz Ledge at the Little Three Mine, Ramona (courtesy of L.B. Spaulding, Jr.). All samples are from the same pocket, and none have been analyzed to date. The tourmaline samples possess sharp euhedral terminations (Fig. 3a) and shiny, striated prism surfaces, but broken fragments show a physically distinct "black" core and "black" jacketing rim (Fig. 3b). Other crystal fragments manifest various degrees of dissolution of the core tourmaline only (Figs. 3c-d), up to complete dissolution leaving hollow crystal sections (Fig. 3e). There is nothing in these samples to suggest that the cores were filled with anything but tourmaline. Where dissolved, the tourmaline has recrystallized euhedral terminations projecting into the central voids from the caps.

Figure 4 is a pink tourmaline crystal with a dark greenish blue jacket and cap from the Elizabeth R. mine, Pala (courtesy of Roland Reed). The pink core of the tourmaline is extensively replaced by lepidolite, which is evident as reflective cleavage flakes parallel to the [0001] growth direction, but the dark jacket shows no alteration. A backscattered electron image of a similar crystal (Fig. 5) shows the core tourmaline, partial replacement by lepidolite, and a void where the micaceous material plucked out between the partially replaced core and the unaltered cap (and jacket). The compositions of the pink core and the blue rim are quite similar; both are fluor-elbaite. One phase was highly susceptible to replacement by lepidolite (and its removal created voids in the core of the crystal), whereas the rim and cap compositions were not.

There is a fundamental theory and quite a bit of published literature on the origins of skeletal crystal growth. I would suggest that interested readers consult the article by Fenn (1986) and then proceed to more theoretical works. The foundation for understanding the selective dissolution and precipitation of minerals in granite-pegmatite systems was presented by Korzhinskii (1959) and applied to granites and pegmatites by Burt (1981). It was used to explain the pseudomorphic alteration of Li-minerals in pegmatites of the White Picacho district, Arizona (London and Burt, 1982a,b), and I have discussed it again in a recent manuscript (submitted to *Lithos*). When a chemical system (e.g., a pegmatite-forming melt ± vapor) is forced to crystallize far from the conditions of its equilibrium, the system tends to oscillate (Nicolis and Prigogine, 1977). That is, it swings from the side of one mineral assemblage to another, and back, as it reacts to approach a state of equilibrium between crystals and melt and/or vapor. In recent papers (e.g., London, 1996), I have suggested that pegmatites represent systems that arise from this process; hence, periods in which a mineral or mineral assemblage is precipitated, then dissolved, then reprecipitated, and so forth, should be prevalent in pegmatites, and they are. Other oscillations that arise from this process include the formation of layered aplite, or “line rock” (e.g., London, 1999). The sharp mineral zonation of pegmatites can promote another episode of alternating dissolution and deposition of the same mineral phase, when at the hydrothermal (e.g., pocket) stage, aqueous fluid can make its way along fractures from one part of the pegmatite to another. Each time a parcel of fluid migrates to a new mineral assemblage, which might be a zone or just a single giant crystal (e.g., of microcline), it will react with that host to approach a new equilibrium composition. As it moves on to another assemblage or mineral environment, it is once again out of equilibrium, and continues to react by dissolving parts of one assemblage and precipitating another…

None of this tells Mr. Rose, precisely, why the tourmaline at the core of his crystal might have dissolved while the rim remained intact, and that is just one of three possibilities proposed so far by Prof. Martin, Dr. White, and myself. If selective dissolution is the cause, then I suggest this may stem from the migration of hydrothermal fluid from pocket to pocket, reacting along the way. Channeled fluid flow (between pockets) and selective scouring and abrasion are evident in the pegmatites of the Little Three mine that I know of. If this hypothesis is correct, then it would suggest the presence of several pockets that became interconnected late in the history of pegmatite consolidation. I hope Mr. Rose can take that as a good omen for further prospecting.

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Figure 1. pseudomorph of quartz, micas and clays after spodumene, 24 cm in length, Bennett Quarry, Buckfield, Maine.

Figure 2. quartz plus molds of albite surrounding voids once filled with spodumene, 13 cm in length, Elizabeth R mine, Pala, California. Traces of dark pink clay (referred to as Li-montmorillonite) remain in the voids.

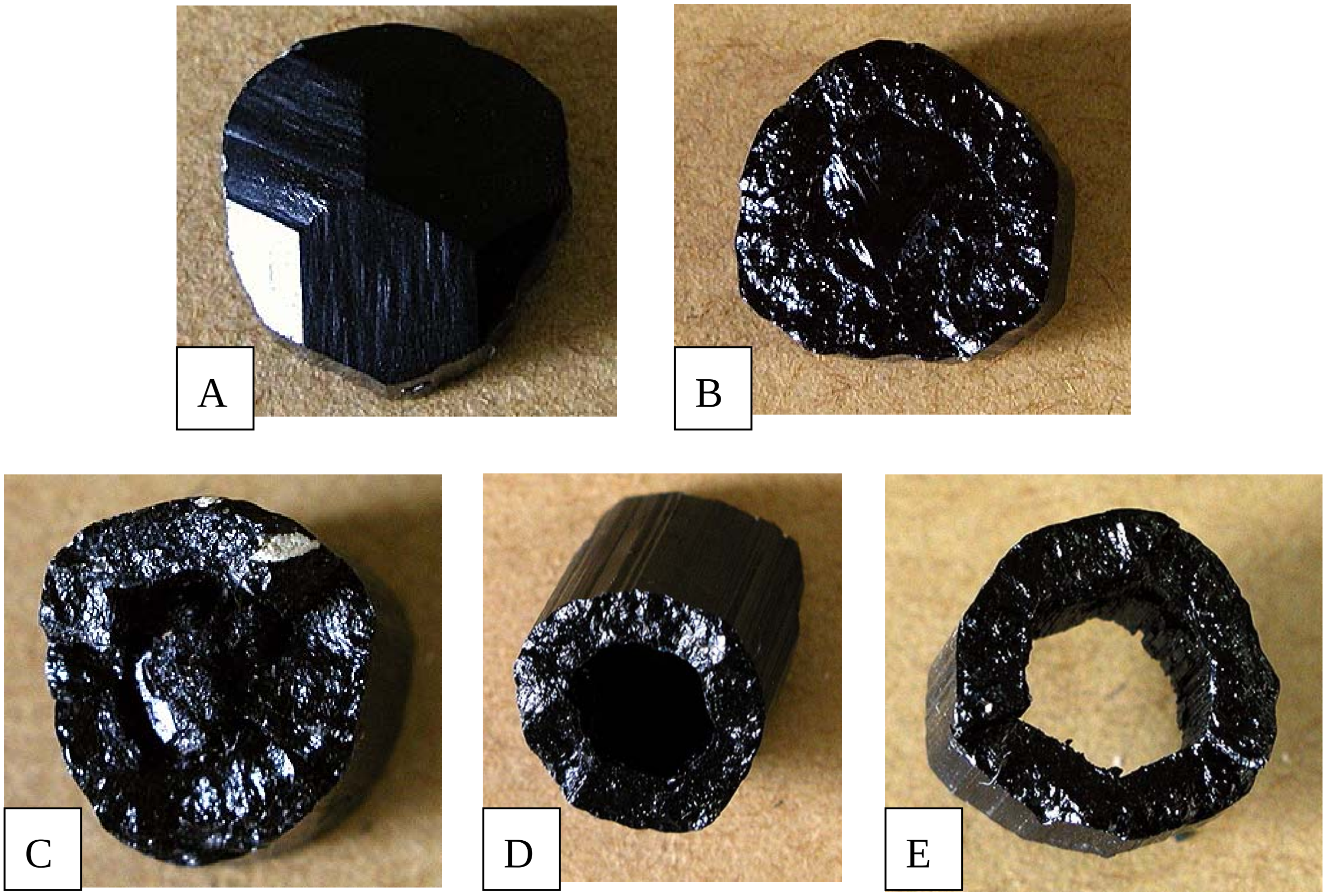

Figure 3. Black tourmaline caps and prisms, Little Three mine, Ramona, California (courtesy of L.B. Spaulding, Jr.). Crystal diameters are ~ 1.5 cm.

Figure 4. zoned blue over pink tourmaline, partially replaced by lepidolite, 7 cm in length, Elizabeth R mine, Pala, California (courtesy of Roland Reed). Traces of dark pink clay (referred to as Li-montmorillonite) remain in the voids.

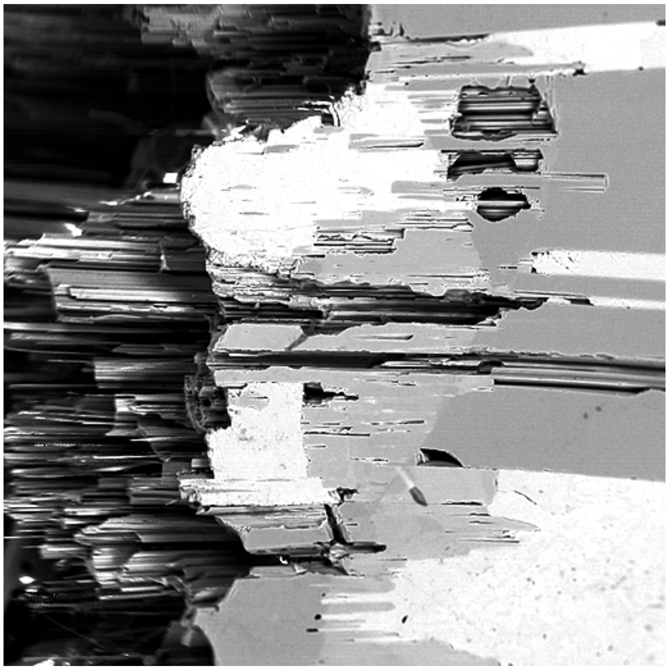

Figure 5. Backscattered electron image of pink and blue tourmaline, Elizabeth R mine, Pala, California (courtesy of Roland Reed). The pink tourmaline of the core is medium-gray, lepidolite is bright white, and the cavity formed by removal of tourmaline and mica is evident toward the left of the photo. Field of view is 1580 x 1580 _m.