

SYNTHESIS OF TOURMALINE BY REACTION OF
MINERAL GRAINS WITH $\text{NaCl-H}_3\text{BO}_3$ SOLUTION,
AND ITS IMPLICATIONS IN ROCK
METAMORPHISM*

CLIFFORD FRONDEL AND R. L. COLLETTE, *Harvard University,*
Cambridge, Massachusetts.

ABSTRACT

Tourmaline can be synthesized by the reaction of a water solution of NaCl and H_3BO_3 on coarse fragments of minerals that contribute the Si, Al and Fe needed in addition to Na, B and OH for the composition of the mineral. The temperature and pressure ranged from 350°C . and 2000 bars to 550° and 700 bars. Most of the common rock-forming minerals were investigated, ranging from mixtures of magnetite, quartz and corundum to mixtures of magnetite with aluminosilicates without additional cations (such as sillimanite) or with additional cations (such as augite). In general tourmaline is not formed if the added minerals contribute alkalis to produce strongly alkaline solutions. A high content of Ca or a high ratio of Ca, Mg and Fe relative to (Al, Si) also is unfavorable.

The formation of tourmaline during the metamorphism of argillaceous sedimentary rocks is discussed from the point of view of Goldschmidt and Peters (1932) and Landergrén (1945) that the boron was originally present in the sediment and not derived from igneous sources.

The ordinary black tourmaline of metamorphic and igneous rocks approximates the composition $\text{NaFe}_3\text{Al}_6(\text{BO}_3)_3(\text{Si}_6\text{O}_{18})(\text{OH})$. Small amounts of K, Ca, Mg, Fe^{3+} and F usually are also present. We have found that tourmaline of this composition is formed by the reaction of a water solution of NaCl and H_3BO_3 at moderate temperatures with pieces of certain minerals that contribute Al, Fe and Si to the system. For example, corundum, magnetite and quartz contribute the Al, Fe, and Si needed for the formation of tourmaline in addition to the Na and B ions present in the solution. This particular mixture produced tourmaline when heated for 72 hours at 700 bars at 550°C . Tourmaline also is formed if NaF is used instead of NaCl . Diaspore used instead of corundum afforded tourmaline at 425° , but not at 350° .

Using a standard run composition, consisting of a water solution 0.3 N in NaCl and 3.0 N in H_3BO_3 together with fragments of magnetite, we have obtained tourmaline using the following aluminum silicates instead of corundum and quartz: sillimanite (at 500° and 460°), kyanite (at 500°), topaz (at 500° , but not 425°), kaolinite (at 550° , 500° and 425° , not 350°), "allophane" (at 550° , doubtfully at 350°) and pyrophyllite (at 550° , 500° and 350° , not 250°). The bomb pressures and run times ranged from 250 bars and 3 days at 550° to 2,000 bars and 7 days

* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 377.

at 350°. Pyrophyllite was much more reactive than the other minerals and afforded the largest tourmaline crystals (about 0.5 mm long at 550° in 10 cc. bomb volume). Addition of quartz to these runs made no significant difference. In these and in the experiments described below the mineral fragments were only superficially attacked and products in addition to tourmaline were present in many instances.

When aluminosilicates that contained additional cations were employed it was found that tourmaline was afforded in some instances but not in others. Using the standard run mentioned above, we obtained tourmaline from staurolite (500°), zoisite (550°, scant at 500°), muscovite (550°, see below), montmorillonite (550°, not 460°), labradorite (rare at 500°, see below), and almandine (500°, not 425°). Grossularite gave negative results at 550°, 500° and 425°, with or without the addition of quartz. Labradorite did not afford tourmaline at 550° or 500°, or when quartz was added, but did yield a very small amount when Al_2O_3 was added. Orthoclase did not give tourmaline at 500°, with or without the addition of SiO_2 or Al_2O_3 . Albite gave negative results at 500°. Biotite, lepidolite and muscovite did not give tourmaline at 500°, or biotite at 550°, but muscovite yielded tourmaline at 550° when SiO_2 was added.

It appears that minerals containing a relatively large amount of alkalis, that react with water to give alkaline solutions, do not form tourmaline under the conditions stated. Thus, in addition to the observations cited above, negative results were obtained from nepheline, sodalite, cancrinite, spodumene and glaucophane. This is further indicated by our (unpublished) observations made on the action of solutions on tourmaline glass and on mixed gels or oxides approximating in composition to tourmaline. Using these starting materials, tourmaline is obtained, depending on temperature and other factors, in weakly alkaline to moderately acid solutions even though alkalis may be present in amounts considerably over the requirements of the formula. The best results are obtained in acid solutions. When the solutions are moderately to strongly alkaline, however, such as by the addition of sodium silicate, sodium carbonate or sodium borates, tourmaline is not formed. It also was found in this connection that runs that produced tourmaline at 500° from pyrophyllite or kaolinite were non-productive when repeated after making the solution 0.1 N in $\text{Na}_2\text{B}_4\text{O}_7$ in addition. In the work of F. G. Smith (1949) on synthesis of tourmaline from its component oxides in water at 400°–500°, the stability field was found to be wholly in the weakly alkaline range in concentrated solutions but with one limit in the weakly acid range in very dilute solutions. The effect of pH may possibly be through an influence on the type of borate anions present in the solution, with (BO_3) groups, such as in the structure of tourmaline, present in the

acid range and $[B(OH)_4]$ or other tetrahedral or polynuclear complexes present in the strongly alkaline range.

Unsuccessful results using the standard run formula were obtained with aluminosilicates relatively high in Mg or Fe^{2+} , including clinocllore and chloritoid, and with aluminosilicates containing Ca together with these cations, including augite and hornblende. An iron-free Mg tourmaline was obtained, however, by using $MgSO_4$ in place of Fe_3O_4 with kaolinite in a stainless steel bomb. A Mg tourmaline also was obtained in a run at 500° that contained SiO_2 , Al_2O_3 , Fe_3O_4 and Mg borate, but not NaCl or H_3BO_3 ; the yield was small, and this interesting tourmaline was not further studied. The negative results obtained with some of the above minerals probably is to be connected with their relatively low content of Al or Si rather than with the content of Mg or Fe.

Stilbite, containing Ca and Na, also gave negative results. Zoisite gave positive results as noted above. Grossularite gave negative results, as did labradorite in the absence of extra Al_2O_3 . A high calcium concentration, or a high ratio of calcium to aluminum, may not be favorable to the formation of tourmaline. Although the bulk of the boron in metamorphosed argillaceous rocks is carried by tourmaline, the boron in highly calcic metamorphic rocks, particularly the crystalline limestones, is distributed among a wide range of species. These include, in addition to magnesium-tourmaline, danburite, serendibite, warwickite, sinhalite, axinite, ludwigite, kotoite and others.

Our experiments suggest that tourmaline can be expected to form in the presence of Na and borate ions during the metamorphism of argillaceous sedimentary rocks, and by the action of these ions on even the high grade equivalents of such rocks. The introduction of boron from igneous sources has been a traditional explanation for the formation of tourmaline in metamorphic terranes. The tourmaline, however, also may originate from boron contained originally in the sediment itself. The work of Goldschmidt and Peters (1932) and of Landergren (1945) on the geochemistry of boron has shown that argillaceous sedimentary rocks are enriched in this element, and it is present in the average amount of 0.03–0.05 per cent B_2O_3 in marine sediments. Pieruccini (1950) found 0.03 to 0.15 per cent B_2O_3 in certain marine clays. The bulk of the boron in these sediments is not contained in accessory detrital minerals such as tourmaline, but apparently is acquired from solution in the sea water by the sediment and is held by adsorption. With increasing temperature the boron may become available to interstitial solutions, such as through desorption attending grain growth, or by recovery from solid solution in unstable phases during their recrystallization, and these solutions may then react with the aluminosilicates to form tourmaline as we have found experimentally.

This general view was first expressed by Goldschmidt and Peters (1932), and has found support in field studies of tourmaline-bearing metamorphosed sediments in central Sweden by Hjelmqvist (1938) and in Greenland by Ellitsgaard-Rasmussen (1954). Aspects of this matter have been discussed by M. C. Michel-Lévy (1953) in light of her work on the hydrothermal synthesis of tourmaline. We have synthesized tourmaline by heating shale (the Cambridge slate in the Boston area) together with magnetite and a water solution of NaCl and H_3BO_3 at 500° and at 650° C. under a pressure of 250 bars. Mme. Michel-Lévy (1949) heated schist at 400° and 10 bars in potassium borate solution and obtained sericite and tourmaline. Crystallization of tourmaline also can take place at relatively low temperatures in view of the wide occurrence of authigenic tourmaline in unmetamorphosed sedimentary rocks. Secondary polar enlargements of tourmaline grains similar to those of sedimentary rocks are readily obtained experimentally by placing seed crystals into hydrothermal syntheses of the nature described.

Tourmaline also can be produced in metamorphic or other rocks by boron introduced from outside sources, as is evidenced, for example, by the tourmaline-rich zones up to a foot or so in thickness that sometimes border large granite pegmatites in the New England area. Hutton (1939) has concluded from field evidence that the boron of the tourmaline in the Otago schists of New Zealand is not of sedimentary origin but has been derived in most instances from deep-seated granitic intrusives. Since borates in general are relatively soluble, particularly the alkali borates, the development of tourmaline during metamorphism also may be viewed as a metasomatic process in which the boron was transported from a more or less distant but not necessarily igneous source. There is, too, the possibility that boron originally present in the sediment may have been removed in solution before the metamorphism reached sufficient intensity to produce tourmaline. The boron might also become tied up in solid solution in an early-formed phase during recrystallization and rendered unavailable over the existence range of that phase. A trace element housed in solid solution in such a phase becomes available to interstitial solutions only when it is later brought into the crystal-solution interface by dissolution or recrystallization of the host crystal.

The tourmaline present in the small, discontinuous pegmatitic veinlets found in many moderate to high grade metamorphic rocks certainly in itself is not critical evidence of the introduction of these pegmatites from igneous sources. They may be authigenic pegmatites derived together with their boron content during the metamorphic process.

ACKNOWLEDGMENTS

We acknowledge with gratitude a critical reading of the manuscript by

Professor James B. Thompson. The experimental work mentioned herein was done in 1948 in connection with Contract W36-039-SC-32153, on the synthesis of tourmaline single-crystals, with the Frequency Control Branch, U. S. Signal Corps, Fort Monmouth, New Jersey.

REFERENCES

- ELLITSGAARD-RASMUSSEN, K. (1954), On the geology of a metamorphic complex in West Greenland. *Medd. om Grønland*, **136**, no. 6.
- GOLDSCHMIDT, V. M., AND PETERS, C. (1932), The chemistry of boron, II. *Nachr. Ges. Wiss. Göttingen, Math. Phys. Kl.*, **28**, no. 31.
- HJELMQVIST, S. (1938), On sedimentary rocks in the leptite formation of central Sweden. *Sverig. Geol. Undersök.*, Sect. C, 413.
- HUTTON, C. O. (1939), The significance of tourmaline in the Otago schists. *Trans. Roy. Soc. New Zealand*, **68**, 599.
- LANDERGREN, S. (1945), Contribution to the geochemistry of boron, II. *Arkiv. Kemi, Min., Geol.*, **19A**, no. 26.
- MICHEL-LÉVY, M. C. (1949), Synthesis of tourmaline and jeremejevite. *C. R.*, **228**, 1814.
- (1953), Artificial reproduction of minerals and comparison of their occurrence in metamorphic rocks. *Bull. soc. min.*, **76**, 237.
- PIERUCCINI, R. (1950), Occurrence of boron in clays. *Per. Min.* **19**, 209.
- SMITH, F. G. (1949), Transport and deposition of the non-sulfide vein minerals. IV. Tourmaline. *Econ. Geol.*, **44**, 186.