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The Incongruent Melting and Crystallization Behavior of Amphibole: A Second Peritectic Reaction in Bowen's Reaction Series and Its Petrogenetic Consequences

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JAMES S. BEARD

ABSTRACT

The reaction of pyroxene plus melt to form amphibole was recognized by Bowen in his earliest depictions of the reaction series. This reaction was included primarily on the basis of observations of amphibole reaction rims about pyroxene. However, the nature of the amphibole-forming reaction was not known to Bowen. Experimental and geochemical work completed since the late 1980s has now identified this reaction, known as dehydration melting, as a peritectic reaction whereby amphibole melts incongruently to form an anhydrous phase assemblage, mostly pyroxene, coexisting with a hydrous, but water-undersaturated melt. It is analogous to the incongruent melting of Mg-Fe pyroxene that was first documented by Bowen himself. Bowen's reaction series is integral to most introductory geology (and virtually all introductory petrology) curricula. This latterday documentation of a second peritectic reaction in the series is a powerful proof-of-concept that further validates the importance and relevance of the reaction series as a pedagogic tool. The peritectic behavior of amphibole has been shown to have important implications for the genesis, crystallization, hybridization, and fractionation behavior of magmas. These include the genesis of silicic magmas, the behavior of water during crystallization and the chemistry of fractionating systems. Thus, the exploration of the petrological consequences of incongruent melting behavior of amphibole also has a place for discussion in (at least) higher level petrology classes.

Key words: peritectic, amphibole, Bowen's reaction series

BOWEN'S REACTION SERIES

The reaction series (now widely known as Bowen's reaction series) was conceived by N.L. Bowen (1922, 1928) as a graphical means to characterize the changes in mineralogy that occur during the fractional crystallization of a basaltic magma. In 1980, Hans Eugster, Bowen's biographer, noted that the reaction series had "found its way into every text on igneous petrology" (Eugster, 1980). Nothing much has changed since 1980, as the reaction series is still presented not only in most introductory geology texts, in print or online (see Johnson et al. (2017) for a typical example), but in

virtually every introductory discussion of igneous petrogenesis in classrooms around the world.

Bowen based the series on a combination of experimental results and observations of natural igneous rocks. Bowen's reaction series is presented as a branched diagram, with one branch (continuous reaction) representing changes in plagioclase composition while a second branch (discontinuous reaction) represents changes in mafic mineralogy (Figure 1).

The continuous series reflects the changes in plagioclase composition during crystallization from more calcium rich to more sodium rich as

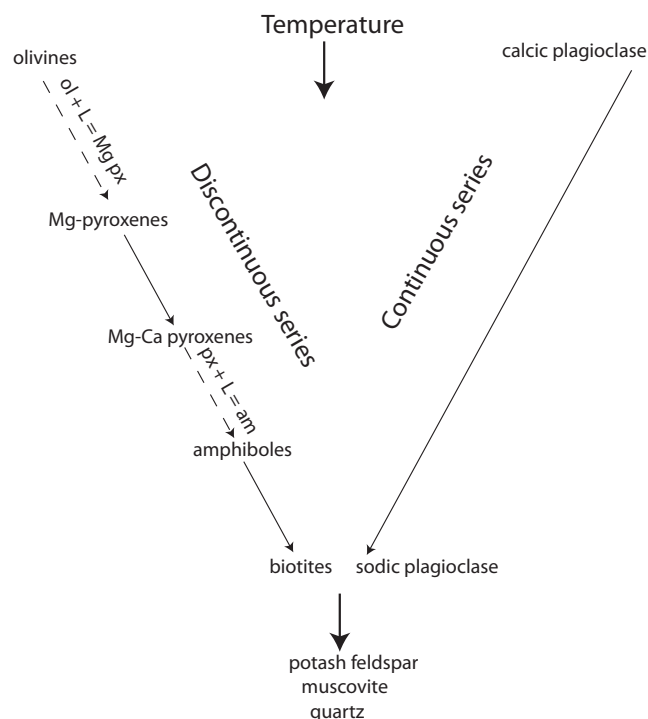


Figure 1. Bowen's Reaction Series after Bowen (1928). The peritectic reactions in the discontinuous series are labeled and shown by dashed lines. Note the addition of $px + melt = am$ as a new peritectic reaction.

temperature decreases. Bowen was well aware of this behavior, both from his own experiments (Bowen, 1913) and from the observation of zoned plagioclase in igneous rocks (Figure 2A). In particular, plagioclase zoning in igneous rocks reflects the early, high-temperature crystallization of calcic feldspar preserved in the cores of zoned crystals vs. later, more sodic feldspar that occurs at the rims of zoned crystals.

The discontinuous series is more complex and it includes some simplifications as well as observations not constrained by experiment in Bowen's time. In particular, Bowen placed Mg-pyroxenes immediately below olivine in the series because of the well-documented peritectic reaction relationship between those two phases (Bowen and Anderson, 1914) (Figure 2B). He placed Mg-Ca pyroxenes next in the series, although he acknowledged that Mg-Ca pyroxenes could occur in a rock with olivine, but lacking Mg-pyroxene (e.g. Table 1 in Bowen, 1928). He correctly inferred that this was a function of bulk composition related to phase behavior in the system forsterite-silica-

diopside. The position of the next mineral in the discontinuous series—amphibole—was inferred (in part) from direct observation of amphibole coronas mantling pyroxene (Figure 2C). The exact nature of this amphibole-pyroxene reaction, however, was not known to Bowen and not experimentally documented until the late 1980s—nearly 70 years after the reaction series was first postulated. It is this reaction that is the focus of this commentary.

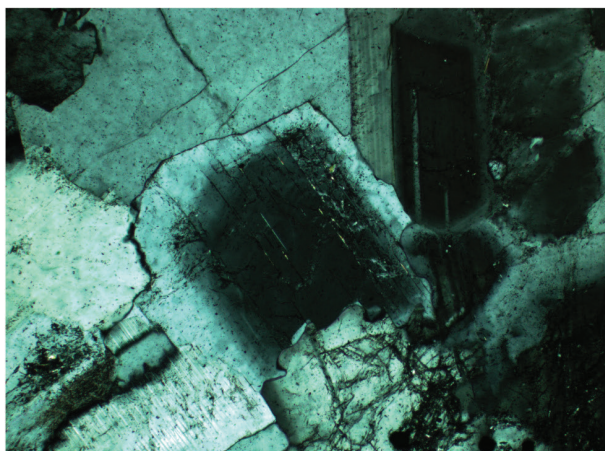
DEHYDRATION MELTING: THE INCONGRUENT MELTING OF AMPHIBOLE

Dehydration melting (Thompson, 1982), is the incongruent, vapor-absent melting of a hydrous phase (mica or amphibole) to yield an anhydrous mineral assemblage coexisting with a hydrous, but water-undersaturated, melt (e.g. Beard et al. 2004). Dehydration-melting of amphibole was documented in a series of experimental studies published in the late 1980s early and mid-1990s (Beard and Lofgren, 1991; Wolf and Wyllie, 1991; 1994, Rapp, Watson and Miller, 1991; Rapp and Watson, 1995; Rushmer, 1991; Skjerlie and Johnston, 1992; Patino Douce and Beard, 1995). The dehydration melting of amphibole can be summarized as: amphibole \pm qtz = pyroxene + hydrous, dacitic melt.

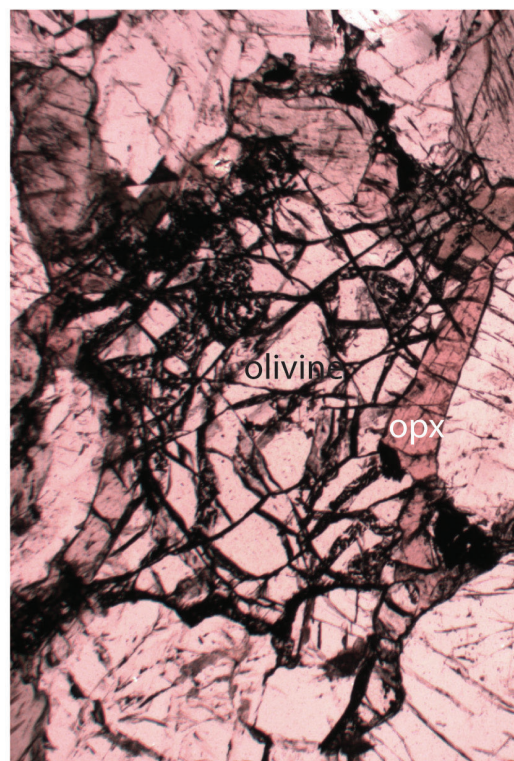
Given the compositional complexity of hornblende amphibole, the actual reaction tends to be more complicated. Depending on various factors (bulk composition in particular), the reaction may be accompanied by changes in plagioclase composition and by the formation of other anhydrous phases, particularly Fe-Ti oxides. It is also now known that the reaction occurs over a range of temperatures, with amphibole composition changing as melt fraction increases (Patino Douce and Beard, 1995). Note also that at pressures above 8 kbar, garnet becomes an important part of the anhydrous phase assemblage (Rapp et al., 1991; Wolf and Wyllie, 1991).

Dehydration melting (in particular, as opposed to water-saturated melting) was shown to be a mechanism to generate dacitic magmas with compositions similar to those observed in island arcs and ophiolites (Beard and Lofgren, 1991) or, at higher pressure with garnet stable, Archaean

A



B



C

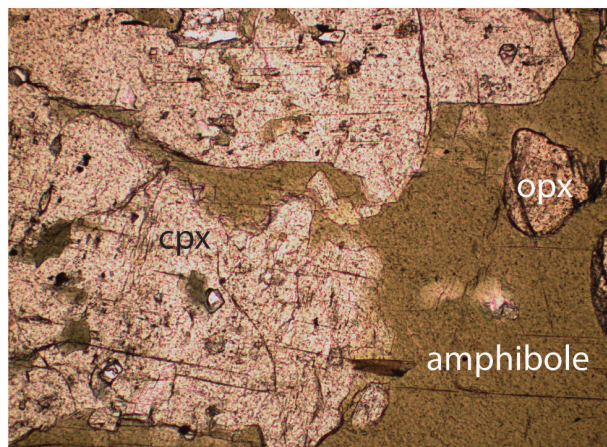


Figure 2. Petrographic manifestations of the reaction series. A.) Plagioclase zoned from a calcic (dark) core to a sodic rim. B.) Olivine with an orthopyroxene (opx) rim, a manifestation of the peritectic reaction $ol + melt = opx$. C.) Clinopyroxene (cpx) and orthopyroxene (opx) partially replaced by amphibole, a manifestation of the peritectic reaction simplified as $pyroxene + \text{hydrous melt} = \text{amphibole}$.

tonalites (Rapp et al. 1991). This work and that which succeeded it throughout the 1990s was focused almost entirely on dehydration melting as a mechanism for tonalite/trondhjemite petrogenesis and little thought was given to other implications of this reaction. In particular the implications of the reaction for magma crystallization were unexplored. Furthermore, even though dehydration melting—where a hydrous mineral breaks down to form a hydrous melt coexisting with an anhydrous mineral assemblage—is obviously an incongruent melting reaction, it was not explicitly described as such at the time (e.g. Vielzeuf and Schmidt, 2001).

HYDRATION CRYSTALLIZATION

The down-temperature, amphibole-forming part of the incongruent reaction is termed “hydration crystallization” (Beard, Ragland, and Rushmer, 2004). Hydration crystallization is the process that produces the amphibole rims on pyroxene that are nearly ubiquitous in calc-alkaline gabbros and diorites (Figure 2C). It was the petrographic observation of these “coronas” that led Bowen to propose a reaction relationship between pyroxene and amphibole. In particular, Bowen (1928) recognized that these coronas could not form by simple hydration of pyroxene, but that a melt had

to be involved to account for the compositional difference between amphibole and pyroxene. For example, a prediction from reaction stoichiometry is that any reaction that forms amphibole (typical $\text{SiO}_2 < 48\%$) from pyroxene (typical $\text{SiO}_2 > 50\%$) must yield free silica while extracting alkalis from the melt. The exploration of this reaction in light of both the results of dehydration melting experiments and petrographic observation has led to insights concerning the late-stage crystallization of magmas. Most critically, the reaction presents a new way to view the late stage crystallization of rocks. Magmatic chemical differentiation trends produced by the peritectic crystallization of amphibole are very different from, for example, those produced by the direct crystallization and fractionation of amphibole (Beard et al., 2004; Beard, Ragland and Crawford, 2005a). In addition, the reaction has the capacity to buffer the water content of a melt, always to the point of minimizing melt water concentration and even to the point (in theory) of precluding water saturation altogether (Beard et al. 2004). These implications remain to be fully explored.

PEDAGOGIC AND PETROLOGIC IMPORTANCE OF A “NEW” REACTION IN BOWEN’S REACTION SERIES

Two mineral-melt reactions were explicitly defined in Bowen’s original series. These are the continuous reaction of plagioclase with melt to produce increasingly sodic compositions down temperature and the peritectic reaction of olivine and melt to produce Mg-pyroxene. The other reactions, including the reaction by which amphibole forms

from pyroxene plus melt, are inferred. In essence, the argument here is that we now can and should acknowledge the peritectic reaction generalized as $\text{pyroxene} + \text{melt} = \text{amphibole}$ in any discussion of Bowen’s reaction series (Figure 1). First, the amphibole reaction validates the concept of a reaction series, in the strict sense, by providing an additional quantified example of a mineral-melt reaction. Second, it emphasizes the value of petrographic observation (e.g. amphibole mantles on pyroxene), indicating that it is a useful first-order tool for describing the chemical behavior of magmas. Finally, it reinforces the value of fact-based intuition in science. Bowen extrapolated the reaction series to amphiboles on the basis of his observations of natural rocks and his knowledge of experiment-based phase petrology. In essence, the peritectic behavior of amphibole was predicted by and is a proof-of-concept for Bowen’s reaction series.

Beyond this, the importance of the incongruent dehydration melting of amphibole, both in terms of the direct generation of dacitic magmas and in terms of the facilitation of bulk assimilation and magma hybridization is widely recognized (Beard and Lofgren, 1991; Rapp and Watson, 1995; Vielzeuf and Schmidt, 2001; Otamendi et al., 2009). As an indication of this, Google Scholar documents over 2,200 citations for the Rapp and Watson paper, nearly 1,000 for the Beard and Lofgren paper, and hundreds of citations each for many other dehydration-melting papers published between 1989 and 1997. A discussion of the petrogenetic importance of the reaction in its own right certainly deserves a place in, at least, advanced petrology classes.

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