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## **7. K-DIFFERENTIATION BY MAGMATIC AND METASOMATIC PROCESSES**

**Lorence G. Collins**

**email: [lorencecollins@gmail.com](mailto:lorencecollins@gmail.com)**

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The granitic crust began to form about 2.5 billion years ago when potassium (K) was abundantly released from the mantle and rose toward the Earth's surface. Today, the mantle still contains about 0.79% K<sub>2</sub>O below 120 km depth, but between depths of 40 to 120 km, the mantle is depleted in K, containing only about 0.10% K<sub>2</sub>O. Above 40 km depth, the average K<sub>2</sub>O content increases gradually to about 3.5% at the Earth's surface (Larin, 1992).

Upward movement of escaping water and other volatile gases from the mantle likely initiated and enabled K-differentiation during Precambrian time. Both magmatic and metasomatic processes in the crust have subsequently further enhanced this differentiation. In magmatic processes, dense, early-crystallized pyroxenes, olivine, and calcic plagioclase, which lack K, settle to the bottom of magma chambers, and left-over melts containing K were displaced upward to the chamber tops. In this way, K was concentrated there to form biotite-bearing gabbro, diorite, and/or tonalite or biotite- and K-feldspar-bearing granodiorite, quartz monzonite, and/or granite. The combination of all these upward K-displacements (differentiation) resulted in more felsic and K-rich rocks at higher levels in the Earth's crust and more mafic and K-poor rocks at lower levels.

Further enrichment of K also occurs in late stages of magma crystallization. Residual hydrothermal fluids, enriched in K, Na, and Fe relative to Mg and Ca, can carry K upward along boundaries of early-formed crystals or through fractures in already crystallized portions of a pluton. The K in such hydrous fluids can replace early-crystallized plagioclase to form K-feldspar which could grow to become megacrysts. In rocks still containing left-over melt, the replacement of the plagioclase crystals by K-feldspar occurs along margins (outside) the plagioclase crystals and then inward (Wadsworth, 1968). Space for the expanded K-feldspar lattice is no problem in this exterior replacement because the adjacent melt provides room into which the K-feldspar can expand. Such replacements can occur on a large scale in a magmatic environment as is illustrated in copper-bearing porphyry granites in Arizona (Wadsworth, 1968).

Another way in which hydrous fluids can create large-scale K-metasomatism is in the late stages of a crystallizing magma during "retrograde boiling." That is, at shallow levels in the Earth's crust, the precipitation of anhydrous minerals, such as quartz and feldspars, may concentrate water in the residual melt so that the water pressure becomes equal to or greater than the confining pressure, and then retrograde boiling occurs. During this boiling, the upward escape of vapors and K-bearing aqueous fluids could further enrich the top of a magma chamber

in K, or if these fluids escape the chamber, they can even metasomatize overlying sedimentary rocks; see later discussion of the Serpent Formation.

At any rate, upward-migrating hydrous fluids, whether produced by retrograde boiling or not, can form K-feldspar crystallizing from the residual melt, with or without replacement of plagioclase. In still later stages at lower temperatures near complete solidification, these K-bearing fluids could cause deuteric alterations or autometamorphism. In that process, some of the migrating K-bearing hydrous fluids might penetrate zoned plagioclase crystals and replace their relatively calcic cores with sericite mica, and the compositional changes would then be almost isochemical. All of these kinds of upward K-differentiation movements would be on a plutonic scale and would be associated with magmatism in early, middle, and late stages of crystallization of a pluton.

After cooling and total crystallization of the magma, temperatures could rise again and cause renewed melting and further upward K-differentiation. This occurs because the first melt that forms during anatexis is enriched in K, and if this partial melt is squeezed upward, the amounts of K would be still further increased at higher levels in the Earth's crust.

The late crystallization of K-bearing minerals in melts and the opposite temperature trend of early melting of K-bearing minerals are thoroughly supported by experimental studies of natural and artificial granites that have been melted and crystallized in closed systems (Tuttle and Bowen, 1958; Luth et al., 1964). The data from these experimental studies show that granitic compositions plot near lowest-temperature eutectics of phase diagrams. Because most natural granites have compositions that plot near eutectic points, many petrologists conclude that the bulk chemical content of all granites of plutonic size must be controlled by the sequence in which minerals first melt or the sequence in which minerals first crystallize and fractionally settle from a melt. Therefore, these petrologists oppose the formation of granite plutons by subsolidus replacement processes. They also argue that subsolidus metasomatism on a large scale to produce granite is not possible because many granites are homogeneous, and supposed replacing fluids are likely heterogeneous.

However, the aforesaid experimental studies do not prove that natural granite compositions that plot near eutectic points must all arrive at these compositions via magmatic processes (Collins, 1994). The compositions of granites at eutectic points merely represent composition stability and do not stipulate the path to this stability.

Homogeneous granite bodies formed by subsolidus replacement processes may be homogeneous precisely because their parent mafic igneous rocks were also homogeneous, just as in the copper-bearing porphyry granites that are formed by K-replacements at temperatures above the solidus. Moreover, the minerals in granite that would be formed by subsolidus replacement processes in an open system (in which myrmekite is formed) would be the same minerals that occur in granite that crystallize from melts because these minerals are stable in the same temperature range. Furthermore, heterogeneous fluids can still make homogeneous granites by subsolidus replacement processes because only certain replacement reactions are possible regardless of the composition of introduced fluids, and these replacements progressively lead to the stable mineralogy which commonly has compositions close to that which plots near eutectic

points. The high-temperature ferromagnesian silicates are replaced by quartz, and the high-temperature, more-calcic plagioclase is replaced by K-feldspar, more-sodic plagioclase, and myrmekite. The replacements by quartz means that Si-metasomatism accompanies K-metasomatism and may be prior to and continuing with K-metasomatism, but Si-metasomatism will not be discussed in this presentation.

In contrast to exterior replacements of plagioclase by K-feldspar in a melt, in a completely solid rock where a plagioclase crystal is confined under pressure by adjacent crystals, the K-feldspar lattice cannot expand against or into the adjacent minerals as it replaces the plagioclase lattice. That is, the K-feldspar cannot forcibly make room for itself by pushing aside the crystals that border the plagioclase as it can by pushing aside a liquid in a melt which can flow and escape the system. Instead, the subsolidus K-replacement of plagioclase is made possible because Ca, Na, and some Al are dissolved out of the dense plagioclase lattice to make room for the expanded lattice of the K-feldspar. Therefore, subsolidus K-feldspar replacements are from the interior outward and commonly begin in the cores of plagioclase crystals because the relatively calcic cores are the least stable in subsolidus T-P conditions. Moreover, the solid nature of the rock means that some sealed (unbroken) surfaces do not have access to the fluids where full exchange of elements is possible, and, thereby, myrmekite may form. In contrast, where full exchange is possible, as occurs where K-feldspar replaces plagioclase in a melt, no myrmekite is formed (e.g., Wadsworth, 1968).

Let's first look at an example of low-temperature, large-scale K-metasomatism in sedimentary rocks. The example occurs in shale from the Proterozoic Serpent Formation of the Huronian Supergroup which extends for thousands of square kilometers in the southern province of the Canadian Shield. This shale contains kaolinite which was derived from weathering of plagioclase-bearing igneous rocks, transported by stream erosion to a rift basin, and deposited in layers whose total thickness is 1 km or more. Later in the geologic history of this formation, hot, K-bearing brines were introduced and replaced much of the kaolinite to form K-bearing illite (Fedo and Young, 1996).

On the basis of the large areal extent and volume of this K-metasomatism of kaolinite in the Serpent Formation, it is reasonable to suggest that similar large-scale metasomatism can also affect solidified igneous rocks, provided that these rocks are deformed or fractured so that K-bearing fluids can be introduced. The source of the K can be from the mantle, from buried biotite-rich metasedimentary rocks, or from biotite-rich mafic igneous rocks. It should be emphasized here that the apparent abundant upward K-differentiation that began 2.5 billion years ago and continued through Precambrian time should be an ongoing process that continues to the present.

Rocks most susceptible to deformation and, therefore, to K-metasomatism are those that contain biotite because it has a hardness of 3 on the Moh's hardness scale and is readily cleavable. The occurrence of abundant biotite in a tonalite, diorite, or gabbro pluton makes such rocks easily deformed, whereas other plutons, which contain abundant hornblende, pyroxenes, or olivine that lack platy cleavage and have hardness greater than 6, are less susceptible to deformation. Moreover, biotite is the only ferromagnesian silicate to contain abundant K, so the deformation and breakdown of biotite results in the release of this element to fluids moving

through the deformed rocks. On that basis, deformed biotite-rich rocks (igneous or metasedimentary) are the likely sources of K to produce K-feldspar in quartz monzonite, granodiorite, and granite that are formed by replacement processes.

Other rocks that are easily deformed are igneous masses that have a circular cross-section and which rise as diapirs, such as the Papoose Flat pluton in California (Sylvester, 1978), or the Ardara pluton in northwest Ireland (Pitcher and Berger, 1972). The strong deformation of solidified margins of these magmatic bodies during their ascent as diapirs would permit K-bearing fluids to rise and move through and around deformed minerals, replacing early-formed plagioclase crystals to produce K-feldspar megacrysts. These replacements could be during late magmatic stages or be subsolidus, following magmatism, particularly where myrmekite is formed.

Strong planar deformation zones in other igneous masses subjected to faulting, shear, or transpression can also permit K-metasomatism so that K-feldspar augen gneisses or foliated megacrystal granites are formed. Examples are the Main Donegal Granite in Ireland (Pitcher and Berger, 1972) and the eastern margin of the Waldoboro granite complex in Maine, U.S.A. (Barton and Sidle, 1994). Therefore, any holocrystalline granitic rock in which possible magmatic (?) foliation is found, should be suspected of being further modified by K-metasomatism. This possibility is because the deformation fabrics (foliation planes and/or lineation) are generally preserved only in late stages of crystallization and because the deformation may continue after the igneous rock has completely crystallized. In either melt or subsolidus conditions, K-bearing hydrous fluids could move through these zones of deformation and convert the magmatic rocks by metasomatism into rocks which are more granitic in composition than their protoliths.

In terranes where this K-metasomatism and differentiation have been operating since the Precambrian, repeated cycles of magmatism, deformation, metasomatism, and re-melting can change former biotite-rich tonalite, diorite, or gabbro, first to granodiorite or quartz monzonite, and then in subsequent cycles to granite. In contrast, the more-competent, hornblende and pyroxene tonalite, diorite, and gabbro that are less easily re-melted or deformed would tend to be preserved. Because of the possibility that biotite-bearing rocks have been subjected to many cycles of magmatism, deformation, metasomatism, and re-melting, this may explain why very few biotite-rich mafic igneous rocks of Precambrian age remain exposed at the Earth's surface. Most have been converted to K-feldspar-bearing granitic rocks.

Because granitic compositions melt at lower temperatures than mafic compositions, melting temperatures are commonly reached in many terranes after K-metasomatism has occurred. The renewed melting destroys the evidence for earlier metasomatism, such as the presence of myrmekite, and these rocks again are magmatic. Moreover, there is no way of distinguishing such rocks formed by a prior history of metasomatism from other granodiorites, monzonites, and granites whose origin is strictly by magmatic processes. Nevertheless, the evidence exists that some granites have formed as a result of K-metasomatism on a plutonic scale, either in late magmatic stages or at subsolidus conditions, and myrmekite is the clue to a subsolidus metasomatic history. Subsolidus K-metasomatism may be so slight that it is almost isochemical, producing only traces of K-feldspar and rim myrmekite, or it can be very extensive,

forming abundant K-feldspar, wartlike myrmekite, sodic plagioclase, and quartz that nearly completely replace the minerals in a former mafic rock. The amount of subsolidus K-metasomatism depends upon the degree of deformation and the availability of K.

Finally, there remains the problem of accounting for the elements that are displaced during subsolidus K-metasomatism on a plutonic scale. This is an issue raised by some petrologists, citing it as an argument against the possibility of forming granite bodies by subsolidus replacement. The supposed problems of a source of abundant K, sufficient volumes of water, and accounting for where displaced Ca, Mg, Fe, and some Al have gone are presumed to make the formation of metasomatic granite plutons unlikely. But these problems also exist in the formation of copper-bearing porphyry granites where K-metasomatism occurs in magmatic rocks on a large scale. Obviously, we need to look for some answers.

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