# Reports

## Cation Diffusion in Plagioclase Feldspar

Abstract. *Steep compositional gradients in igneous plagioclase feldspar from slowly cooled intrusive bodies imply a maximum value of the intracrystalline diffusion coefficient for NaSi $\rightleftarrows$ CaAl exchange, $D_{max}$ ~$10^{-20}$ centimeters squared per second for temperatures in the range 1250° to 1000°C. Millimeter-sized grains cannot be homogenized in all geologic time; hence reactive equilibrium crystallization of plagioclase from the melt does not occur in dry systems.*

The plagioclase feldspars, $CaAl_2Si_2O_8$ (anorthite, An)–$NaAlSi_3O_8$ (albite, Ab), form a continuous solid solution series at high temperatures. They are the most common minerals in the crust, and major schemes of rock classification are based on their composition. Since Bowen's 1913 study (*1*) they have formed the foundation of experimental igneous petrology. Bowen considered two limiting, idealized processes of crystallization in the plagioclase system: perfect fractional and perfect (reactive) equilibrium crystallization. In the former, crystals are continuously separated from melt by zoning or removal and the residual liquid is rapidly enriched in the low-melting component Ab (*2*). In the equilibrium case, the coupled cation-exchange reaction $(NaSi)^{5+} \rightleftarrows (CaAl)^{5+}$ hypothetically occurs between crystal and liquid during slow crystallization to produce a single homogeneous composition at the end of crystallization. Zoned crystals and phenocrysts of plagioclase illustrate fractional crystallization and have been exploited to unravel complex mixing histories of volcanic magmas (*3*). However, the existence of zoned plagioclase in deep-seated, slowly crystallized rocks, whose cooling rates can be estimated at 100° to 10,000°C per $10^6$ years, is in itself strong evidence against intracrystalline diffusion involving the NaSi $\rightleftarrows$ CaAl exchange couple (*4, 5*). The relevant diffusion coefficients are difficult to measure experimentally. By applying geologic limits of time, temperature, and length scale, diffusion rates can be estimated to show why the limiting equilibrium case earlier considered by Bowen does not, in fact, occur in dry magmas.

Large areas of homogeneous crystals in deep-seated layered intrusions (*6*) are thought to have grown at constant temperature and composition by diffusive exchange of pore magma with an effectively infinite reservoir of fresh magma, a process called adcumulus growth (*7*). Zoned crystals in such bodies are conventionally interpreted as local fractionation products resulting from the isolation and later polythermal crystallization of trapped liquid. Recent observations on such plagioclase-rich cumulates have shown the profusion if not ubiquity of narrow "reversed" (that is, CaAl-rich, nominally "higher temperature") rims on some crystals (*8, 9*). These rims are igneous products, not the result of later reactions in the solid state (*10*). The composition gradients of an extreme example are shown in Fig. 1. At the most strongly zoned rim, the crystal composition changes from $An_{57}$ (that is, An/(An + Ab) = 0.57 or 57 percent) to $An_{90}$ over a distance of 40 μm. Along the same profile, the potassium concentration changes from >2000 ppm (by weight) to <100 ppm, and the K/Na ratio drops by a factor of 6 (Fig. 1b).

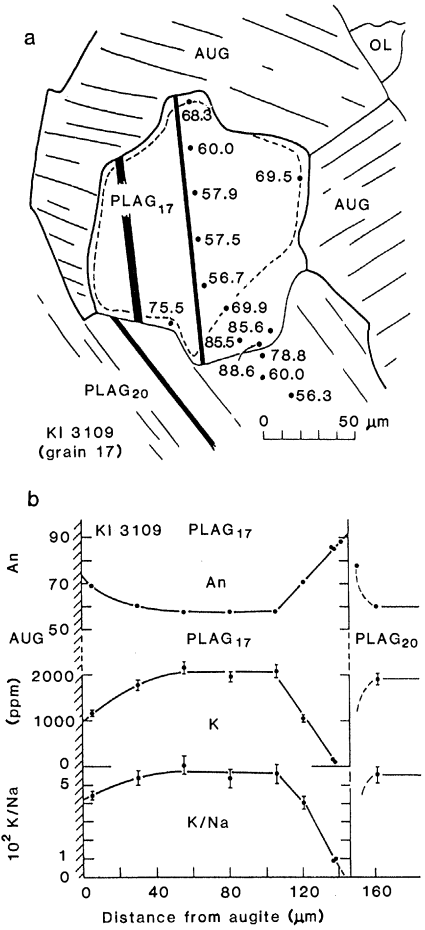

Fig. 1. (a) Map of plagioclase crystal 17, showing compositions in mole percent An ($CaAl_2Si_2O_8$) relative to An + Ab ($NaAlSi_3O_8$) along a north-south traverse; sample KI 3109 from the basal lower zone of the Kiglapait intrusion, Labrador (*11, 12*). Abbreviations: PLAG, plagioclase; AUG, augite; OL, olivine. (b) Composition profiles along the same traverse; all data were obtained by electron probe microanalysis.

This example comes from an olivine-plagioclase rock (troctolite) in the basal few hundred meters of the large, Precambrian Kiglapait layered intrusion in Labrador (*11*). Similar reversed rims, commonly 5 to 10 μm wide but as narrow as 2 μm, have been observed in each of hundreds of troctolite samples examined, from stratigraphic levels at least as high as 5 km above the base of the intrusion. The inferred temperature range for the crystallization of the entire body is 1250° to 960°C, and the inferred crystallization time is $10^6$ years (*12*). Samples from the interior of the intrusion have been annealed above 1000°C for an estimated (0.5 ± 0.1) × $10^6$ years. The retention of zoning implies failure of complete equilibration by internal diffusion and hence implies an upper limit to the diffusion coefficient D for intracrystalline NaSi $\rightleftarrows$ CaAl exchange. This value, $D_{max}$, can be estimated by the well-known Einstein approximation as $D_{max} \sim x^2/t$, where $x$ is the characteristic transport distance and $t$ is time. Choosing $x$ as 5 μm ($5 \times 10^{-4}$ cm) and $t$ as $0.5 \times 10^6$ years ($1.58 \times 10^{13}$ seconds), we find that $D_{max}$ is ~$1.6 \times 10^{-20}$ cm$^2$ sec$^{-1}$. The calculation is not critically dependent on the choice of $t$: if the cooling time above 1000°C is anywhere between $0.3 \times 10^6$ years and the maximum of $1.0 \times 10^6$ years, the value of $D_{max}$ is still ~$10^{-20}$ cm$^2$ sec$^{-1}$. The crystals were actually cooled over a temperature range from about 1250° to 1000°C; thus the estimate refers to the mean diffusion coefficient over that temperature interval. It is clear that a plagioclase crystal as small as 0.1 cm in diameter would not be homogenized by internal diffusion at or above 1000°C in less than about $10^{10}$ years or, in other words, not in all of geologic time (~$4.5 \times 10^9$ years).

The exercise above yields a formally maximum D because diffusion has not removed the zoning. Demonstration of a minimum transport distance would yield a formally minimum value of D. Feldspars near the top of the Kiglapait intrusion provide a useful basis for estimating such a lower limit. These are ternary (Ca,Na,K) feldspars initially crystallized as a homogeneous phase (*8*) but now exsolved into irregular, spindly lamellae of coexisting plagioclase ($\sim$An$_{17}$) and calcium-free orthoclase of differing Al/Si ratio. Photos of such "mesoperthites" are shown in plate 48 of Morse (*11*). The typical lamella width is 1 to 2 μm. If the feldspar components have been segregated by volume diffusion rather than growth at a propagating tip, the characteristic diffusion distance is about $10^{-4}$ cm. The interval over which segregation might have occurred is at maximum 950°C to 460°C, the former being the estimated crystallization temperature (*12*) and the latter the minimum blocking temperature for diffusion in feldspar (*13*). A cooling rate of 8500°C per $10^6$ years is estimated (*12*) for the late-stage crystallization history of the intrusion, and, because this stage is dominated by the specific heat rather than the latent heat of crystallization, this cooling rate is extended to the subsolidus cooling history, yielding an annealing time of $\sim 65 \times 10^3$ years above 460°C. For $x = 10^{-4}$ cm, $D_{\mathrm{min}} = 5 \times 10^{-21}$ cm$^2$ sec$^{-1}$. The actual blocking temperature was probably higher than 460°C, so the diffusion coefficient and the mean temperature to which it applies could both be higher, hence closer to the maximum estimate.

An estimate of D for the NaSi $\rightleftarrows$ CaAl exchange was made by Grove *et al.* (*14*), based on interpretations of experimental studies at high temperature and metamorphic mineral textures at low temperature. They deduced Arrhenius constants to imply $D \sim 1.4 \times 10^{-20}$ cm$^2$ sec$^{-1}$ referred to a temperature of 1000°C, a result very similar to the values obtained here.

Feldspars are framework silicates in which the small cations Al$^{3+}$ and Si$^{4+}$ occupy tetrahedral sites coordinated to four oxygens, and Ca$^{2+}$, Na$^+$, and K$^+$ occupy more open, polycoordinated VII- to IX-fold sites. Because of the relatively high diffusivity of alkali cations in calcium-free feldspar (*13*), it is classically and no doubt correctly considered that nontetrahedral cations are exchanged with relative ease. The resistance of the NaSi $\rightleftarrows$ CaAl couple to diffusion is therefore to be laid at the door of the tetrahedrally coordinated and more strongly bonded Al $\rightleftarrows$ Si exchange, which is the rate-limiting step in the observed nondiffusion (*4, 5*). Remarkably, the observed K/Na gradient shown in Fig. 1b implies that the K $\rightleftarrows$ Na exchange in plagioclase (as contrasted with alkali feldspar) is rate-limited by the tetrahedral Al $\rightleftarrows$ Si exchange as well, at least at these low potassium concentrations. If so, this limitation would imply that the substitution of potassium for sodium in plagioclase requires a special site related to the local tetrahedral Al/Si distribution. Alternatively, the observed K/Na gradient could reflect a solubility gradient at constant chemical potential, although the available data do not suggest such a low solubility limit of potassium in calcic plagioclase (*15*).

The Kiglapait intrusion affords a useful limiting case because of its vanishingly low $H_2O$ content (*16*), since $H_2O$ is known to act as a catalyst to diffusion in some types of feldspar (*5, 17*). However, delicately zoned plagioclase feldspars are known from more hydrous, large granitic intrusions (*18*), and it is possible that, even in the presence of $H_2O$ dissolved in the magma, the intracrystalline cation diffusion rate is not markedly enhanced.

The inferred low value of D explains why plagioclase feldspars are such good recorders of thermal and compositional environments in deep-seated igneous rocks. Bowen's reactive equilibrium crystallization cannot be correctly invoked to explain the homogeneous plagioclase crystals of submillimeter to meter size found in unmetamorphosed mafic igneous rocks such as anorthosite, norite, troctolite, and gabbro (*19*). Steady-state growth at constant composition (that is, adcumulus growth) must be inferred instead for such examples of homogeneous plagioclase.

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### References and Notes

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## Sinking of Volcanic Ash in Uncompacted Sediment in Williams Lake, Washington

Abstract. *Volcanic ash from the eruption of Mount St. Helens on 18 May 1980 fell into Williams Lake in eastern Washington and was temporarily suspended at the sediment-water interface. After several months of compaction, the ash layer broke up and sank into lower density uncompacted lake sediment. Stratigraphic time displacements of several hundred years and a failure to recognize discontinuous ash layers in sediment cores are possible consequences of this process.*

The ash from the 18 May 1980 eruption of Mount St. Helens settled into several lakes that were under the plume of tephra as it passed over south-central and eastern Washington (Fig. 1). The ash was subsequently compacted and the ash layer broke up and sank into the sediment beneath the ash.

The 18 May event provides an opportunity to examine the sinking of an ash layer in detail. For example, Welch *et al.* (*1, 2*) showed that an ash layer 3- to 4-cm thick in the deeper part of Moses Lake (reservoir), Washington, broke up after deposition and sank 5 to 6 cm below the sediment-water interface. The compacted ash layer in Williams Lake is 1.5 to 2 cm thick and in places has sunk nearly 1 m below the sediment-water interface.

Piston and gravity cores containing the 18 May ash layer were collected from various depths in Williams Lake in July 1983. In addition, the sedimentation rate in the lake has been measured by automated sediment traps since 7 August 1980. The information obtained is used to examine the rate of sinking of the ash and to estimate the chronostratigra-