

Silica solid solution and zoning in natural plagioclase

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Abstract

Microprobe analyses of plagioclase from some lunar basalts have anomalous stoichiometry as compared to terrestrial feldspars. The anomaly indicates the presence of the "excess silica" substitution, $[\text{Si}_4\text{O}_8]$. This coupled substitution leaves a vacancy in the feldspar lattice and is effectively SiO_2 dissolved in the feldspar. Detailed study indicates that core-rim $[\text{Si}_4\text{O}_8]$ zoning is a common phenomenon in plagioclase from lunar basalts. Anorthite-albite zoning is also typically present, so plots of $[\text{Si}_4\text{O}_8]$ as a function of anorthite content provide a convenient measure of the $[\text{Si}_4\text{O}_8]$ variations present. Most lunar basaltic plagioclase shows a monotonic increase in $[\text{Si}_4\text{O}_8]$ with albite content, typically ranging from 0 mole percent $[\text{Si}_4\text{O}_8]$ in the cores to 5-7 percent in the rims. This zoning is produced by two cooperating processes: a falling temperature of formation, and growth from a progressively siliceous liquid. In addition, rapid growth and delayed nucleation of plagioclase and silica phase appear to be important to the disequilibrium incorporation of $[\text{Si}_4\text{O}_8]$.

By contrast, plagioclase from a wide variety of terrestrial occurrences lacks $[\text{Si}_4\text{O}_8]$. The absence of $[\text{Si}_4\text{O}_8]$ in many terrestrial igneous plagioclases is primarily related to the presence of H_2O , which decreases the liquidus temperatures relative to those in lunar rocks. Terrestrial basalts which have comparable crystallization temperatures to their lunar counterparts lack $[\text{Si}_4\text{O}_8]$ in part because of an absence of strong *in situ* differentiation. In addition, plagioclase typically crystallizes prior to pyroxene (the reverse of the mare basalts), so kinetic effects have a reduced role. If a melt is in equilibrium with cristobalite (or tridymite or quartz), the silica activity is buffered, and the $[\text{Si}_4\text{O}_8]$ content of the plagioclase is directly related to the temperature. $[\text{Si}_4\text{O}_8]$ incorporation, however, is typically not an equilibrium process, so there is little hope of using it directly as a geothermometer.

Introduction

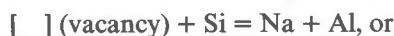
This paper is concerned with the extent and significance of silica solid solution in natural plagioclase, a subject which has had a long history in the geological literature. Myrmekite was thought by Schwantke (1909) and Phillips (1964) to have formed by the subsolidus unmixing of feldspar and a dissolved silica-rich component. The first discoveries of excess silica in natural feldspars were those of Chayes and Zies (1962) and Carmen and Tuttle (1963, 1967), in sanidine from rhyolites. Luth and Tuttle (1966), however, found no evidence for excess silica in alkali feldspars (mostly microcline and orthoclase) from a wide variety of geologic environments. Wyart and Sabatier (1965), Kim and Burley (1971), Orville (1972), Bruno

and Facchinelli (1974), Ito (1976), and Longhi and Hays (1979) all succeeded in producing excess-silica-bearing feldspars in the laboratory, including both anorthite and albite. The Longhi and Hays study presented the $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-SiO}_2$ phase diagram, laying the foundation for the interpretation of excess silica in natural feldspars. Consistent with the idea of silica solid solution is the fact that feldspar has a structure polytypic to that of coesite (Megaw, 1970; Thompson and Hovis, 1979), a condition favoring mutual solubility.

The first demonstration of excess silica in natural plagioclase came from studies of the lunar samples (e.g., Weill *et al.*, 1970). Many workers noted that some lunar plagioclase analyses differed in stoichiometry from their terrestrial counterparts. The "anomalous" analyses had too much Si, too little Al, and a deficiency of the singly- and doubly-charged

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cations which fill the larger site (Table 1). Wenk and Wilde (1973) and Longhi *et al.* (1976a) demonstrated that the feldspar substitution $[\]\text{Si}_4\text{O}_8$ is necessary to balance these anomalous analyses. This coupled substitution,



is hereafter referred to as the excess silica substitution. By routinely calculating the amount of $[\]\text{Si}_4\text{O}_8$ in plagioclase analyses from the Apollo 11 basalts, Beaty and Albee (1978) discovered well-defined core-rim excess silica zoning in single crystals. Subsequent studies of other groups of lunar basalts (Beaty and Albee, 1979; Beaty *et al.*, 1979a, b, c; Baldrige *et al.*, 1979) showed that $[\]\text{Si}_4\text{O}_8$ zoning is a common phenomenon in lunar plagioclase. Our purpose is to synthesize these data, supplement them with new analyses from other rock types and other geologic environments, and develop a meaningful

picture of the extent, causes, and significance of silica solid solution and zoning in plagioclase.

Analytical techniques

Small variations in the amount of any of the major cations can drastically effect the amount of excess silica which is subsequently calculated. Systematic differences, such as those introduced by using different analytical methods or even the same method but different instruments, may affect the excess silica values. For this reason, we have used only data collected on the Caltech microprobe. Analyses for all elements were performed consecutively on a single spot with a MAC-5-SA3 electron microprobe interfaced to a PDP-8/L computer for on-line control and data processing. Operating conditions were uniformly 15 kV accelerating voltage and either 0.05 or 0.005 μA sample current (on brass) with beam current integration and pulse height selection. Elements with peak to background ratios greater than five (about 1 weight percent of the oxide) are counted to a precision of 1% or better. Minor elements (<1 percent abundances) are usually counted for 90 seconds, which yields counting statistics of better than 10% for elements present in amounts greater than ~0.1 weight percent. Reproducibility (1σ) on two "known unknowns" over a 13-month period ranged from 1.5 (for elements with abundances >1 percent) to 3 percent of the amount present (for elements with abundances >0.1 percent) (Champion *et al.*, 1975).

All plagioclase analyses were normalized to 16 positive charges (assuming ferrous iron), and then the formulae calculated in the following manner. First, the tetrahedral site was filled by making $\text{Ca}(\text{Fe},\text{Mg})\text{Si}_3\text{O}_8 = 4 - (\text{Si} + \text{Al})$. Next, we set $\text{KAlSi}_3\text{O}_8 = \text{K}$, $\text{NaAlSi}_3\text{O}_8 = \text{Na}$, $\text{BaAl}_2\text{Si}_2\text{O}_8 = \text{Ba}$, $\text{CaAl}_2\text{Si}_2\text{O}_8 = \text{Ca} - \text{Ca}(\text{Fm},\text{Mg})\text{Si}_3\text{O}_8$, $(\text{Fe},\text{Mg})\text{Al}_2\text{Si}_2\text{O}_8 = \text{Mg} + \text{Fe} - \text{Ca}(\text{Fe},\text{Mg})\text{Si}_3\text{O}_8$, and finally $[\]\text{Si}_4\text{O}_8 = 1 - [\text{Na} + \text{Mg} + \text{K} + \text{Ca} + \text{Fe} + \text{Ba} - \text{Ca}(\text{Fe},\text{Mg})\text{Si}_3\text{O}_8]$. Ti was measured but ignored; in basaltic plagioclase it is typically 0.05–0.10 weight percent (Table 1), which would decrease the calculated excess silica by 0.2–0.3 mole percent. The calculated uncertainties (1σ , using Bernoulli counting statistics) for this algorithm are ± 0.2 mole percent for the An content, and ± 1.5 mole percent for the excess silica.

The tetrahedral Fe calculation $[\text{Ca}(\text{FeSi}_3)\text{O}_8]$ is based on spectroscopic experiments. Mössbauer studies by Hafner *et al.* (1971) and Appleman *et al.* (1971) suggest that, in Apollo 11 and 12 plagioclase at room temperature, 20–60% of the Fe^{2+} is in tet-

Table 1. Representative plagioclase analyses

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
SiO_2	50.98	52.75	50.46	51.76	50.48	49.89	50.67	52.26
TiO_2	0.12	0.09	0.12	0.01	0.11	0.08	0.21	0.25
Al_2O_3	31.29	29.72	30.88	30.51	31.06	32.07	29.37	29.05
MgO	0.03	0.10	0.20	0.14	0.14	0.10	0.30	0.42
CaO	14.54	13.07	14.27	13.72	14.91	16.07	16.56	15.35
FeO	0.45	0.64	0.50	0.54	0.86	0.85	1.63	1.51
Na_2O	3.24	3.96	3.81	4.12	2.18	1.90	1.39	1.71
K_2O	0.16	0.22	0.18	0.18	0.24	0.08	0.09	0.08
BaO	0.02	0.04	<.01	<.01	<.01	<.01	<.01	0.13
Σ	100.83	100.59	100.42	100.98	99.98	101.04	100.22	100.76
Number of cations normalized to 8 oxygens								
Si	2.310	2.388	2.302	2.340	2.307	2.262	2.326	2.376
Ti	0.004	0.003	0.004	0.000	0.004	0.003	0.007	0.009
Al	1.672	1.586	1.661	1.626	1.674	1.714	1.590	1.557
Mg	0.002	0.007	0.014	0.009	0.010	0.007	0.021	0.028
Ca	0.706	0.634	0.698	0.665	0.730	0.781	0.815	0.748
Fe	0.017	0.024	0.019	0.020	0.033	0.032	0.063	0.057
Na	0.285	0.348	0.337	0.361	0.193	0.167	0.124	0.151
K	0.009	0.013	0.010	0.010	0.014	0.005	0.005	0.005
Ba	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.002
End-member abundances								
$\text{KFe}^{3+}\text{Si}_3\text{O}_8$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
KAlSi_3O_8	0.9	1.3	1.0	1.0	1.4	0.5	0.5	0.5
$\text{NaAlSi}_3\text{O}_8$	28.4	34.8	32.3	34.9	19.3	16.7	12.4	15.1
$\text{BaAl}_2\text{Si}_2\text{O}_8$	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.2
$\text{CaAl}_2\text{Si}_2\text{O}_8$	68.7	60.8	63.6	61.3	71.0	75.6	73.2	68.0
$\text{FmAl}_2\text{Si}_2\text{O}_8$	0.1	0.5	0.0	0.0	2.3	1.5	0.0	1.8
$\text{CaFmSi}_3\text{O}_8$	1.8	2.6	3.1	2.9	2.0	2.4	8.3	6.8
$[\]\text{Si}_4\text{O}_8$	0.0	0.0	0.0	0.0	4.0	3.3	5.6	7.6

(1)–(2) Skaergaard intrusion (unpub. data from R. Gregory); (3)–(4) New Mexico basalt (unpub. data from W. S. Baldrige); (5)–(6) 10047 (Beaty and Albee, 1978); (7)–(8) 70215 (Dymek *et al.*, 1975).

rahedral coordination. Although these results were not confirmed in a near-infrared spectral study (using Luna 20 material) by Bell and Mao (1973), Sclar and Kastelik (1979) were able to synthesize a complete isostructural series ranging in composition from $\text{CaAl}_2\text{Si}_2\text{O}_8$ to $\text{CaFeSi}_3\text{O}_8$. Furthermore, Wenk and Wilde (1973), Longhi *et al.* (1976a,b), and our studies all indicate that both $[\]\text{Si}_4\text{O}_8$ and $\text{Ca}(\text{Mg,Fe})\text{Si}_3\text{O}_8$ are necessary to balance lunar plagioclase analyses. Note, however, that the $[\]\text{Si}_4\text{O}_8$ calculation is independent of site-occupancy assumptions, depending only on the total number of cations. If ferric iron were present in a plagioclase crystal, the amount of excess silica calculated using the above method would be about 0.1 mole percent less than that actually present for every 0.5 weight percent Fe_2O_3 .

Our analytical technique was cross-checked by analyzing in a single microprobe run a variety of plagioclase samples that had been previously analyzed at different times. By relocating old analysis points we were able to determine our total reproducibility, as well as to directly compare different feldspar analyses. This experiment showed better reproducibility in excess silica determination than the calculated 1.5 mole percent ($\sigma = 0.58$ based on 26 measurements). In addition, our analyses of well-characterized terrestrial plagioclase standards indicated no excess silica, even when analyzed alternately with high- $[\]\text{Si}_4\text{O}_8$ lunar feldspars.

One of our major conclusions is that detectable excess silica is not present in most terrestrial plagioclase. This means that the crystallographic sites are fully occupied. It is equally valid, therefore, that instead of normalizing to a total positive charge of 16, terrestrial feldspar analyses be normalized to 5 total cations. The ferric/ferrous ratio, however, typically cannot be determined from the total positive charge because the uncertainties are too large (see above).

Silica solid solution in natural plagioclase

Apollo 11 low-K basalts

Figure 1 illustrates the compositional dependence of excess silica in plagioclase from three Apollo 11 low-K basalts. In each rock, $[\]\text{Si}_4\text{O}_8$ shows a strong inverse correlation with anorthite content. Plagioclase (An_{91}) is on the liquidus in 10047, and continues to crystallize to the solidus (An_{69}). The first plagioclase to form has no excess silica, but as the rock crystallizes, more and more excess silica is incorporated, reaching a maximum of 4.6 mole percent in the mesostasis areas (Fig. 1). The entire zoning

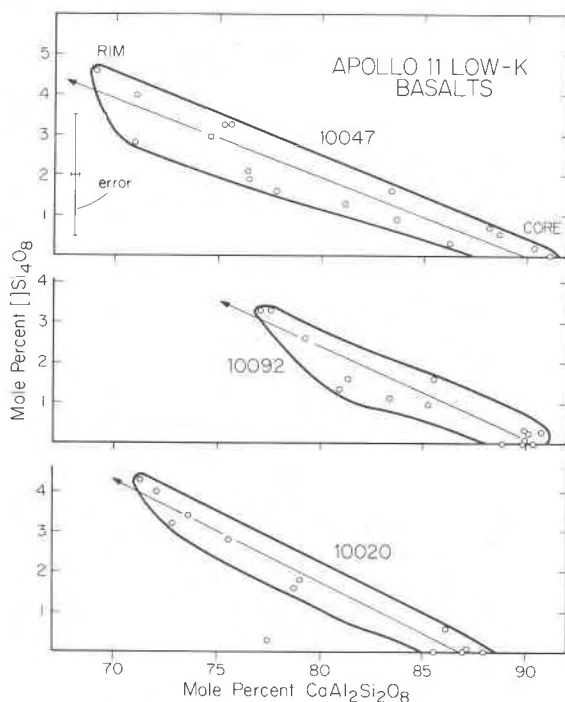


Fig. 1. Variations in $[\]\text{Si}_4\text{O}_8$ as a function of $\text{CaAl}_2\text{Si}_2\text{O}_8$ for plagioclase in Apollo 11 low-K basalts 10047, 10092, and 10020. In each case excess silica increases in a regular way from core to rim of the plagioclase, and the three samples show the same zoning trend. This trend is produced by both falling temperature and *in situ* differentiation. The error bar is the calculated absolute uncertainty, but the reproducibility (width of the data envelopes) is somewhat less.

trend can be found in core-rim profiles of single crystals, and each grain shows the same profile.

10092 and 10020 are much finer-grained than 10047, and in both rocks plagioclase is the third phase to appear on the liquidus (after olivine and spinel). Nevertheless, both samples have excess silica zoning profiles very similar to that of 10047. The principal difference lies in the extent of the zoning; *in situ* differentiation was not as efficient in 10092. The remainder of the Apollo 11 low-K basalts have zoning patterns similar to those in 10047, 10092, and 10020 (Beaty and Albee, 1978; Beaty *et al.*, 1979b).

The simple excess-silica zoning profiles in plagioclase from the low-K basalts can easily be understood in terms of the phase diagram plagioclase- SiO_2 . The An-SiO_2 join of this diagram has been experimentally determined at low pressure by Longhi and Hays (1979) and is reproduced in simplified form in Figure 2. The excess silica substitution is equivalent to SiO_2 dissolved in anorthite and is therefore governed by the univariant curves bounding the anorthite field. At temperatures close to its melting

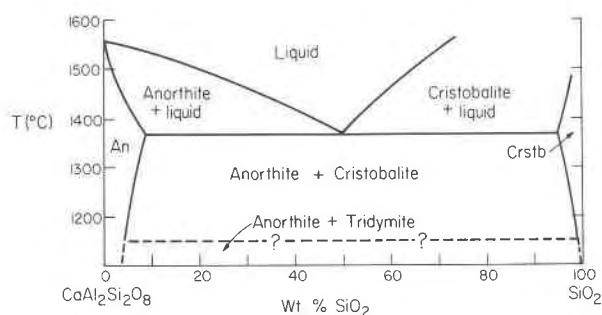


Fig. 2. Experimentally-determined phase diagram for the binary system $\text{CaAl}_2\text{Si}_2\text{O}_8$ - SiO_2 (after Longhi and Hays, in press). The width of the An field determines the maximum solubility of $[\]\text{Si}_4\text{O}_8$ at any given temperature. Additional details involving the silica polymorphs on the right side of the diagram have been omitted for simplicity.

point, anorthite can contain very little dissolved silica. As the temperature falls, the solubility of silica in anorthite steadily increases, reaching a maximum of 9 mole percent $[\]\text{Si}_4\text{O}_8$ (8 weight percent) at 1370°C , the temperature of the anorthite-cristobalite eutectic. With further cooling, the anorthite will progressively lose its $[\]\text{Si}_4\text{O}_8$ to cristobalite, tridymite, and then quartz.

In the Apollo 11 low-K basalts, the first plagioclase crystallized at high temperature from a melt that was marginally quartz-normative. As predicted by the phase diagram, it contains negligible amounts of $[\]\text{Si}_4\text{O}_8$. As the magma cooled it differentiated, and the residual liquid was enriched in SiO_2 . The monotonic increase in $[\]\text{Si}_4\text{O}_8$ from core to rim of the plagioclase crystals is therefore caused by two factors: increasing silica solubility in plagioclase at lower temperatures, and an increasingly siliceous parental melt. Because both temperature and composition determine the amount of $[\]\text{Si}_4\text{O}_8$ incorporated in the feldspar, excess-silica zoning profiles must depend strongly on the liquid line of descent. The fact that all of the Apollo 11 low-K basalts have similar zoning trends therefore indicates that they followed similar liquid lines of descent. This is consistent with the bulk chemical and petrologic similarities present within the suite (Beaty and Albee, 1978).

Apollo 12 pigeonite basalts

Like the low-K basalts, the Apollo 12 pigeonite basalts also show an inverse correlation between $[\]\text{Si}_4\text{O}_8$ and anorthite content (Fig. 3). In each rock, plagioclase rims contain more excess silica than the cores. In contrast to the low-K basalts, however, the several pigeonite basalts do not have similar profiles. 12011 ranges from 3–6 percent $[\]\text{Si}_4\text{O}_8$, 12043 has

from 0–4 percent, and 12007 zones from 0–2 percent (Baldrige *et al.*, 1979). When these excess silica contents are compared to the anorthite contents (Fig. 3), the plagioclase analyses from all three samples fall along a common trend. For the reasons discussed above, the inverse relation between $[\]\text{Si}_4\text{O}_8$ and An content suggests that the three samples crystallized from the same parental liquid along the same liquid line of descent. The different positions along the common trend suggest different positions of plagioclase saturation.

Petrologic evidence indicates that the cooling rate decreases in the order $12011 > 12043 > 12007$ (Baldrige *et al.*, 1979), the same order in which $[\]\text{Si}_4\text{O}_8$ decreases. This correlation is also found in the Apollo 12 feldspathic basalts (Beaty *et al.*, 1979c). Plagioclase saturation occurs after olivine, pigeonite, and augite in these rocks. With increased cooling rate all the saturation temperatures are depressed, but the temperature of plagioclase appearance is depressed most (Walker *et al.*, 1978; Grove and Raudsepp, 1978; Grove and Bence, 1979). Therefore, in the more rapidly cooled samples more of the early ferromagnesian phenocrysts form. This enriches the residual melt in silica, and depletes it in Ca and Al through the incorporation of $\text{CaAl}_2\text{SiO}_6$ in pyroxene. The excess-silica data can therefore be understood in terms of a simple undercooling series. In 12011 plagioclase began crystallizing at a lower temper-

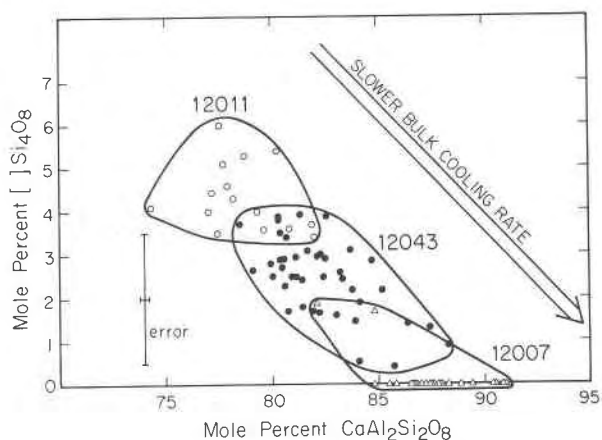


Fig. 3. Excess silica in plagioclase from the Apollo 12 pigeonite basalts. In each sample, single crystals are zoned from calcic $[\]\text{Si}_4\text{O}_8$ -poor cores to sodic $[\]\text{Si}_4\text{O}_8$ -rich rims. Superimposed on this is a cooling rate effect: the slower the rock cooled, the less overall excess silica its feldspar contains. This indicates that kinetic factors are also responsible for the incorporation of excess silica in plagioclase.

ature and from a more siliceous melt than the plagioclase in 12007.

When plagioclase and one of the silica polymorphs are in equilibrium, their compositions are determined by the solvus portion of Figure 2. The position of the solvus is relatively insensitive to the liquid composition (for a more detailed discussion, see below). Therefore, since all the pigeonite basalts are in equilibrium with either cristobalite or tridymite at their solidi, it is theoretically possible to compare solidus temperatures by examining the excess silica contents of the last plagioclase to crystallize. This suggests that 12011, which has more $[\text{Si}_4\text{O}_8]$, had a higher solidus temperature than 12007. Figure 2, however, indicates that this temperature difference would have to be several hundred degrees, which is petrologically unreasonable. This evidence argues that the high $[\text{Si}_4\text{O}_8]$ contents of the more rapidly cooled samples, such as 12011 and 12043, are produced by disequilibrium kinetic factors.

Experimental studies (e.g. Grove and Bence, 1979) show that with increased cooling rates the abundances of the minor constituents increase in each mineral. This is thought to be related to kinetic factors: if the material in the magma at the mineral-melt interface does not have time to diffuse away from the growing crystal, it is incorporated (Albarede and Bottinga, 1972). The high $[\text{Si}_4\text{O}_8]$ contents of 12011 and 12043 may in part be related to this process. Also important is the delayed nucleation of the silica phase (Longhi, personal communication, 1979), which could cause the metastable incorporation of $[\text{Si}_4\text{O}_8]$ in plagioclase in large amounts. The significance of kinetic effects is confirmed by the observation that most lunar basalts have solidi about 1050°C , and at that temperature plagioclase in equilibrium (using Longhi and Hays' Fig. 1) with tridymite contains about 3 mole percent $[\text{Si}_4\text{O}_8]$. The high $[\text{Si}_4\text{O}_8]$ contents of mesostasis plagioclase, therefore, appear to be kinetically controlled.

Apollo 17 basalts

The positive correlation between overall excess silica content and cooling rate is also present in a suite of Apollo 17 basalts (Fig. 4). 70215 contains from 2–7.5 percent $[\text{Si}_4\text{O}_8]$, 74255 has 0–6 percent, 71055 has 1–4 percent, and 75055 ranges from 0–2 percent. According to the petrographic observations of Dymek *et al.* (1975), the cooling rate decreased in the same order (70215 > 74255 > 71055 > 75055). In contrast to the Apollo 12 pigeonite basalt suite, these data do not define a common trend. Unlike the pi-

geonite basalts, however, there is little assurance that these four samples came from the same lava flow. The excess silica data suggests that 70215 and 71055 followed the same liquid line of descent (Fig. 4), but that 74255 crystallized along a different path. Note that each sample considered alone shows the anticipated inverse correlation between $[\text{Si}_4\text{O}_8]$ and anorthite content.

Apollo 15 basalts

We have analyzed plagioclase from three Apollo 15 basalts. In both 15555 and 15682, olivine-normative and quartz-normative samples respectively, the excess silica increases from 0 percent at An_{86} to 4 percent at An_{76} . In common with the Apollo 12 pigeonite basalts, plagioclase was the last major phase to crystallize. The trends suggest similar liquid lines of descent for the two magmas. However, 15976, another quartz-normative basalt, has a maximum of only about 1 mole percent excess silica.

Apollo 11 high-K basalts

Most of the Apollo 11 high-K basalts have plagioclase containing large amounts of excess silica (Beaty and Albee, 1978). In some samples $[\text{Si}_4\text{O}_8]$ is correlated with anorthite content (Fig. 5, 10024, 10017), but in others it is not (e.g. 10072). 10024, the coarsest-grained rock of the suite, ranges from 2–7 percent $[\text{Si}_4\text{O}_8]$ (Fig. 5). In order of decreasing grain size 10072, 10071, 10017, 10069, and 10049 contain 1–4, 0–7, 0–2, 0–1, and 0–7 percent excess silica, respectively. Unlike the Apollo 12 and 17 suites, the overall amount of excess silica is not correlated with the in-

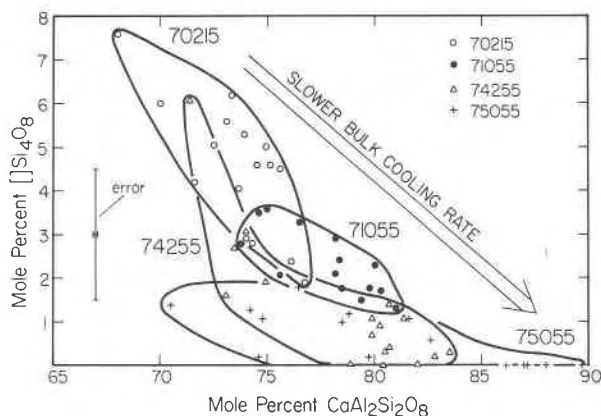


Fig. 4. Excess silica zoning in Apollo 17 basalts. In each sample excess silica increases from core to rim of the plagioclase. As in Apollo 12 basalts (Fig. 3), the bulk cooling rate also affects the amount of excess silica.

ferred cooling rate. Neither does it depend on the bulk composition. In short, the excess silica contents of these samples vary in a way not easily understood in terms of any of the arguments advanced above.

As discussed in the section on Apollo 11 low-K basalts, a natural consequence of the anorthite-SiO₂ phase diagram (Fig. 2) is that the amount of excess silica in plagioclase will steadily increase with crystallization until cristobalite saturation occurs (at the eutectic), where crystallization is completed. In multicomponent systems cristobalite saturation will occur at a cotectic and plagioclase and cristobalite will cocrystallize down the cotectic. As long as the liquid is in equilibrium with both cristobalite and plagioclase, the amount of []Si₄O₈ in the plagioclase will decrease with falling temperature. Thus, []Si₄O₈ reversals ought to be present in the rims of feldspars from cristobalite-bearing lavas. Such reversals were reported for six of the ten Apollo 11 high-K samples (Beaty and Albee, 1978). Reexamination, however, indicates that the data are only suggestive, not conclusive.

Luna 24 and Apollo 14 basalts

In contrast to the above data, several lunar basalts contain little or no excess silica in their plagioclase. Ferrobasalt 24170, for example, has excess silica values close to zero. The data range from 0–2 percent []Si₄O₈, and are scattered with no detectable zoning. Since the data spread is somewhat shifted off zero,

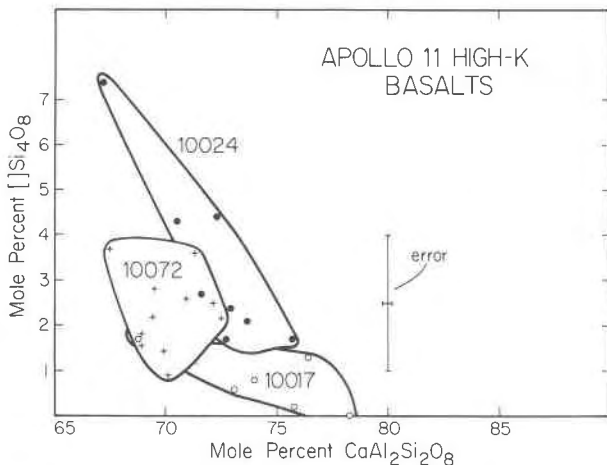


Fig. 5. []Si₄O₈ in plagioclase from the Apollo 11 high-K basalts 10024, 10072, and 10017. Unlike Figs. 3 and 4, there is no correlation with bulk cooling rate; the variations within the suite cannot be related to any known parameter. 10024 and 10017 show the negative correlation between []Si₄O₈ and CaAl₂Si₂O₈ found in plagioclase from most lunar basalts (Figs. 1, 3, and 4).

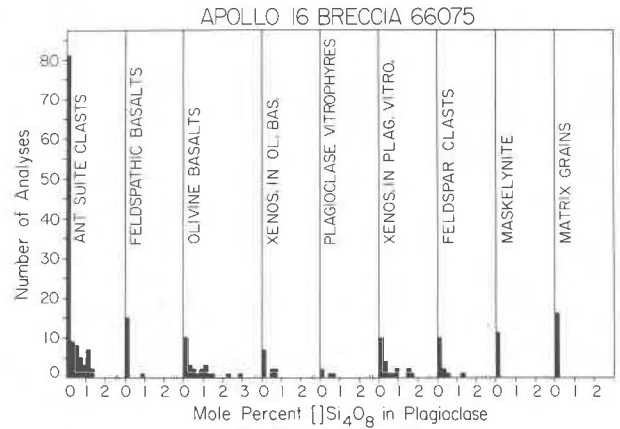


Fig. 6. Excess silica in plagioclase from lunar highlands breccia 66075. Unlike those in the mare basalts, these feldspars are virtually devoid of []Si₄O₈. In all but the olivine basalt clasts the data lie within analytical uncertainty (1.5 mole percent) of zero. These plagioclases are also essentially unzoned (An₉₇₋₉₃). In the olivine basalts, however, the plagioclase is zoned from An₉₄₋₈₃ and from 0–3 percent []Si₄O₈. This illustrates the importance of *in situ* differentiation to the formation of []Si₄O₈.

there is probably a small (~0.5 percent) amount of []Si₄O₈ actually present in the plagioclase. Grove and Bence (1979), however, report that in their dynamic crystallization experiments on a Luna 24 composition, []Si₄O₈ in plagioclase increases from rock to rock with both cooling rate and falling temperature. Like 24170, Apollo 14 basalts 14310 and 14053 also contain very little excess silica.

It is difficult to understand why the plagioclase in these samples contains no excess silica. The pyroxene zoning trends indicate *in situ* differentiation (Gancarz *et al.*, 1971; Wasserburg *et al.*, 1978), and the liquids all became siliceous enough near their solidi to precipitate cristobalite. Furthermore, the parental liquids are thought to have crystallized through temperature intervals (Grove and Vaniman, 1978; Walker *et al.*, 1975) similar to the previously discussed mare basalts. One possible explanation lies in the observation (Longhi, personal communication 1979) that most lunar basalts crystallized pyroxene before plagioclase, whereas in Luna 24 and Apollo 14 plagioclase precedes or is simultaneous with pyroxene. Perhaps the delayed nucleation of plagioclase followed by supersaturation and rapid growth is necessary for the incorporation of large amounts of excess silica.

The lunar highlands (Apollo 16)

There is negligible excess silica in plagioclase from the anorthositic lunar highlands. Quick *et al.* (1978) divided the plagioclase in highlands soil breccia

66075 into nine populations: anorthosite–norite–troctolite (ANT) clasts, feldspathic basalts, olivine basalts, xenoliths in the olivine basalts, plagioclase vitrophyres, xenoliths in the plagioclase vitrophyres, feldspar clasts, maskelynite clasts, and matrix grains. All plagioclases except those from the olivine basalts have compositions in the range An_{93} – An_{97} and excess silica contents of between 0 and 1.3 mole percent (Fig. 6). About 80 percent of these analyses indicate less than 0.2 percent [] Si_4O_8 , and the data spread reflects analytic uncertainty about a true value of zero. In the olivine basalt clasts, however, the plagioclase is zoned from An_{94} to An_{83} and the excess silica increases sympathetically from 0–3 mole percent (Fig. 6). Because the olivine basalts are extremely rare, it is possible to conclude from this that there is no measurable excess silica in the large anorthosite–gabbro masses that make up the lunar highlands.

Both the plagioclase vitrophyres and the olivine basalts are interpreted to be impact melt-rocks (Quick *et al.*, 1978), and as such have undergone similar cooling histories. Both melts were highly olivine-normative and were rapidly cooled from a high temperature under similar conditions. The olivine basalts, however, underwent fractional crystallization to a greater degree than did the plagioclase vitrophyres, as indicated by the more sodic feldspars.

Greater differentiation can also explain the differences in [] Si_4O_8 contents—the more evolved residual liquids in the olivine basalts were probably more siliceous than those in the plagioclase vitrophyres. Consequently, they were able to crystallize more [] Si_4O_8 -rich plagioclase. Study of these melt-rocks, therefore, underlines the importance of *in situ* differentiation to increase [] Si_4O_8 ; it is a common means of producing the necessarily siliceous parental melts.

Terrestrial plagioclase

In contrast to the lunar samples discussed above, none of the terrestrial rocks studied contain [] Si_4O_8 -bearing plagioclase. Figure 7 shows a set of plagioclase analyses from a basalt flow in the Jemez Mountains, New Mexico. Most data indicate a complete absence of [] Si_4O_8 , and all analyses are within the analytical uncertainty of zero. Similar results were obtained from four other basalt flows in the area as well as from tholeiites (Longhi and Hays, 1979).

The differences between these samples and most of the mare basalts are profound. Figure 7 also shows data for the Skaergaard intrusion, probably the best-understood igneous body in world. Like the New Mexican basalts, none of its plagioclase contains measurable amounts of [] Si_4O_8 . Although they are not illustrated, excess silica is also absent in plagioclase

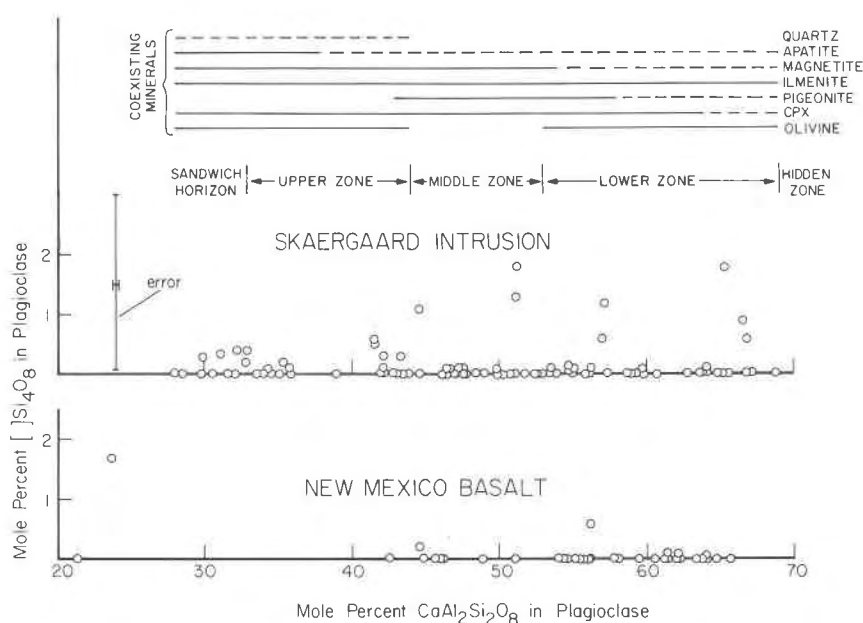


Fig. 7. Excess silica content of plagioclase as a function of anorthite content for the Skaergaard intrusion and a basalt from the Jemez Mountains, New Mexico. Shown for reference are the coexisting minerals of the Skaergaard (solid = cumulus phase, dashed = intercumulus or indeterminate) (Wager and Brown, 1967, p. 26–27). The data represent analytic uncertainty about a value of zero, indicating an absence of [] Si_4O_8 in the plagioclase. This pattern is typical of that found in all terrestrial rocks examined in this study.

clase analyses from amphibolites from Vermont, granulites from Greenland, lherzolite from California, andesite from Paricutin, peridotite xenoliths in New Mexico basalt flows, a granodiorite from Australia, a tonalite from the Baja California batholith, pelitic schists from Death Valley, and arkosic sandstones from California.

Note that if Na and K are lost by volatilization from the volume being analyzed, there will be deficiency in the larger site, and depending on how the end-members are calculated, the resulting composition may have fictitious excess silica. This alkali loss can occur when the electron beam has too small a diameter. Although such analyses need to be eliminated, it is difficult to distinguish genuine excess silica from alkali loss or otherwise bad analyses. Zoning patterns like that in Figure 7, however, lead us to conclude that for the terrestrial samples we have studied, the presence of large amounts (>2 percent) of excess silica is a good criterion for discarding the analysis. Furthermore, none of the high- $[\text{Si}_4\text{O}_8]$ analyses could be reproduced when analyzed a second time.

Discussion of terrestrial data

There are several possible explanations for the absence of $[\text{Si}_4\text{O}_8]$ in terrestrial plagioclase. First of all,

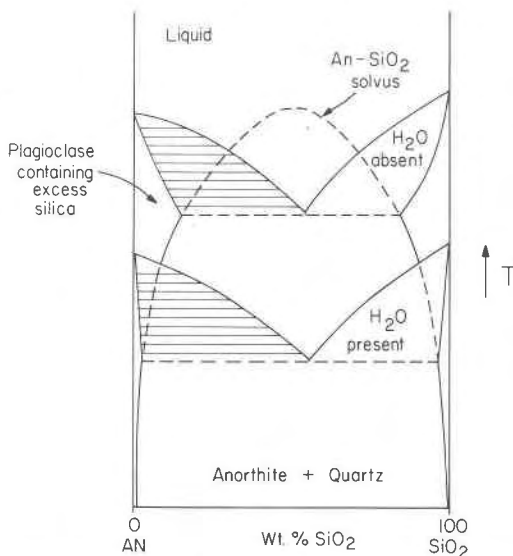


Fig. 8. Schematic phase diagram anorthite-SiO₂ illustrating the effect of adding H₂O. The liquidus is significantly depressed, but the solvus is not affected. This in turn dramatically decreases the amount of $[\text{Si}_4\text{O}_8]$ in the plagioclase (shown by the tie lines). This is one reason why (wet) terrestrial magmas such as the Skaergaard (Fig. 7) have no $[\text{Si}_4\text{O}_8]$, but in equally differentiated (dry) lunar basalts (Figs. 1, 3, 4, and 5) it abounds.

terrestrial basalts typically do not show extensive *in situ* fractional crystallization. As discussed above in connection with Apollo 16, fractional crystallization is essential to the production of $[\text{Si}_4\text{O}_8]$ in basaltic plagioclase. In addition, terrestrial basalts, like Luna 24 and Apollo 14, crystallize plagioclase before pyroxene, so there is less opportunity for delayed nucleation effects to generate $[\text{Si}_4\text{O}_8]$.

The liquid line of descent followed by the Skaergaard as it crystallized, however, was similar to that followed by the lunar mare basalts. The degree of silica saturation increased steadily with fractional crystallization, culminating in quartz precipitation in the Upper Zone and Sandwich Horizon (Fig. 7). Although the liquid paths of the Skaergaard and the lunar basalts were similar chemically, they were different thermally. The lunar basalts were dry, whereas the Skaergaard magma, like all terrestrial magmas, contained a small amount of water, appreciably depressing its liquidus temperature. The plagioclase therefore crystallized at lower temperature, a condition sufficient to cause the plagioclase to incorporate much less $[\text{Si}_4\text{O}_8]$.

This effect is schematically illustrated in Figure 8. As other components, such as albite, orthoclase, pyroxene, olivine, and particularly volatiles, are added to the binary system anorthite-SiO₂ (Figure 2) to make a rock, the liquidus will be depressed to lower temperatures. The effect on the plagioclase-SiO₂ solvus is more difficult to predict. The presence of a component which is insoluble in either anorthite or the SiO₂ polymorphs at all temperatures will not affect the equilibrium between them. The addition of phases like pyroxene, ilmenite and water to the simple binary system, therefore, will closely approximate the behavior shown in Figure 8. The melting loop will be lowered, whereas the solvus will have a nearly constant position independent of the bulk composition.

Varying the albite content of the plagioclase, however, could either increase or decrease the solvus temperature. According to Kim and Burley (1971), albite may contain up to 5 mole percent silica in solid solution at 5.15 kbar and 670°C. From size and charge considerations, albite might be expected to contain more $[\text{Si}_4\text{O}_8]$ than anorthite at any given temperature (J. B. Thompson, personal communication, 1979). Although both albite and anorthite are therefore known to contain excess silica, the detailed shape of the "SiO₂"-plagioclase solvus as a function of plagioclase composition is uncertain. Note that this problem can be avoided by comparing feldspars

of constant albite content. With these limitations in mind, a great deal of insight can be gained from Figure 8.

Figure 8 shows in a schematic way one reason why measurable amounts of $[]\text{Si}_4\text{O}_8$ are not present in the Skaergaard plagioclases. The solubility of silica in plagioclase decreases with temperature, and the temperature interval over which the Skaergaard crystallized was too low for measurable amounts of $[]\text{Si}_4\text{O}_8$. The effect is more important for magmas such as granites and tonalites which have high water contents and even lower crystallization temperatures. A low temperature of formation can also explain why excess silica was not found in any of the metamorphic plagioclase studied. In addition to the temperature effect, terrestrial plutonic feldspar is less subject to the disequilibrium kinetic factors which are important in producing $[]\text{Si}_4\text{O}_8$ in lunar basaltic plagioclase.

Meteorites

We have analyzed plagioclase from the St. Severin chondrite (LL6) and found that it contains no excess silica. The anorthite in the white inclusions in Allende also contain no excess silica (Lee *et al.*, 1977; Bradley *et al.*, 1978). Colomera, an unusual iron meteorite with silicate globules, has both plagioclase and K-feldspar which are $[]\text{Si}_4\text{O}_8$ -free. Using data from other laboratories, Bence and Burnett (1969) reported that crypto-antiperthite from Kodaikanal ranged from 0–4 percent high in SiO_2 . Partial (6-element) analyses of the plagioclase in enstatite chondrites (Keil, 1968) also suggest small amounts of excess silica. The enstatite chondrites are an extremely reduced group containing Si dissolved in the metal (Ringwood, 1961; Keil, 1968). The excess silica in the plagioclase may be related to the presence of elemental silicon. Additional work is necessary to more fully evaluate the $[]\text{Si}_4\text{O}_8$ variations among meteorites.

Excess silica preservation

Most of the preceding discussion has treated the variable incorporation of $[]\text{Si}_4\text{O}_8$ in plagioclase crystals at high temperature. $[]\text{Si}_4\text{O}_8$ may or may not have been preserved as the crystal cooled to room temperature, however. Two mechanisms are available by which the excess silica could be lost: exsolution and diffusion. If the $[]\text{Si}_4\text{O}_8$ were lost by exsolution, a distinctive myrmekite consisting of ~5 percent quartz and 95 percent plagioclase (as opposed to a 50–50 mixture) would be formed. The authors have neither seen such an intergrowth nor are

aware of any reported in the literature. Observation is made more difficult by the uncertainty in distinguishing magmatic from exsolved quartz inclusions (e.g., Walker *et al.*, 1973, p. 1018). Submicroscopic exsolutions may be present, but if so they are in low abundance, otherwise they would show up in the microprobe analyses.

Likewise there is little evidence that $[]\text{Si}_4\text{O}_8$ is lost by diffusion. The excess silica gradients in the Apollo 11 low-K basalts (Fig. 1) show no evidence of being flattened, even in the most slowly cooled samples. Although less $[]\text{Si}_4\text{O}_8$ is contained in the more slowly cooled Apollo 12 and Apollo 17 basalts, this is probably related to the physical conditions of growth rather than diffusive loss (see above). The apparent low diffusion coefficient of $[]\text{Si}_4\text{O}_8$ is related to the fact that it is an integral part of the feldspar structure. In order for $[]\text{Si}_4\text{O}_8$ to be lost, a crystal must both lose Si and gain either Ca and Al or Na and Al, a complicated coupled diffusion process. If such processes were operating the anorthite–albite zoning of the crystals would also be affected. Therefore, any plagioclase grain which has preserved its anorthite–albite zoning might also be expected to preserve its excess silica zoning.

Thus far, excess silica has been confirmed in plagioclase from relatively rapidly cooled lunar volcanic rocks. In the much more slowly cooled plutonic rocks from both the moon and the earth, $[]\text{Si}_4\text{O}_8$ is absent. Plutonic plagioclase is also typically unzoned, hence it is not possible to be certain whether or not $[]\text{Si}_4\text{O}_8$ was originally present.

Summary

Most of the variations in the $[]\text{Si}_4\text{O}_8$ content of natural plagioclase can be understood in terms of a few simple factors. Most importantly, a high temperature of formation and a siliceous parental melt are essential. Excess silica typically increases monotonically from core to rim of the plagioclase in lunar basalts. This trend is caused by two cooperative effects—falling temperature increases the solubility of $[]\text{Si}_4\text{O}_8$ in plagioclase, and fractional crystallization of the melt causes the plagioclase to grow from an increasingly siliceous residual liquid. In addition to these equilibrium processes, delayed nucleation of plagioclase and a silica phase followed by rapid feldspar growth can cause metastable incorporation of $[]\text{Si}_4\text{O}_8$ in large amounts.

These effects are schematically illustrated in Figure 9. Lunar basalts, which crystallize at high temperatures with large degrees of fractional crystalliza-

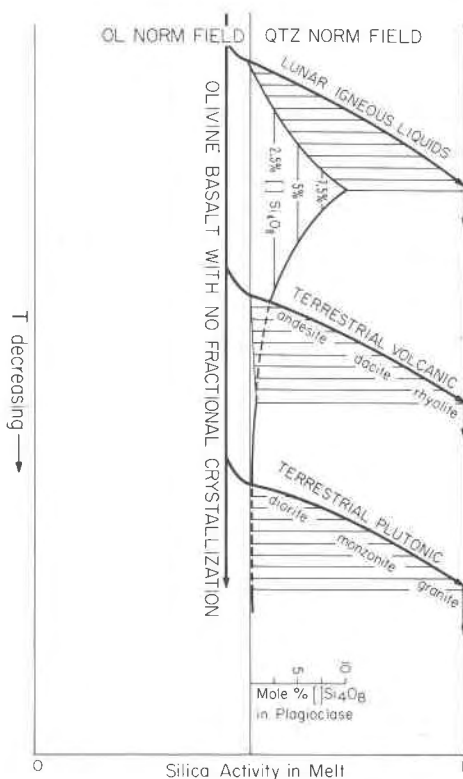


Fig. 9. Schematic diagram showing the relationship between the field of excess silica and natural igneous rocks. By projecting different liquid lines of descent onto this diagram it is possible to illustrate the major factors responsible for the incorporation of $[]\text{Si}_4\text{O}_8$ in plagioclase. If an olivine-normative basalt undergoes no fractional crystallization, it will follow the arrow so labeled and never enter the $[]\text{Si}_4\text{O}_8$ stability field. With differentiation at high temperature (e.g. lunar igneous liquids), much $[]\text{Si}_4\text{O}_8$ will be present. At lower temperatures, the terrestrial volcanic spectrum is expected to have only minor amounts of $[]\text{Si}_4\text{O}_8$. At even lower temperatures, plagioclase in terrestrial plutonic rocks should have even less $[]\text{Si}_4\text{O}_8$. In addition, the delayed nucleation and rapid growth of plagioclase can cause the disequilibrium incorporation of large amounts of $[]\text{Si}_4\text{O}_8$.

tion, contain large amounts of $[]\text{Si}_4\text{O}_8$. The fact that the observed $[]\text{Si}_4\text{O}_8$ concentrations (up to 8%) exceed those predicted by Figure 2 (3%) can be attributed to kinetic effects. In contrast to the lunar basalts, terrestrial basalts have no $[]\text{Si}_4\text{O}_8$ in their plagioclase. This is related to two reasons. First, terrestrial basalts do not show the strong *in situ* differentiation of the lunar basalts—the residual liquids do not have high silica activities. As shown on Figure 9, an olivine basalt which undergoes no fractional crystallization will not enter the $[]\text{Si}_4\text{O}_8$ stability field. In addition, plagioclase crystallizes before pyroxene in most terrestrial basalts, reducing the possibility of metastable

$[]\text{Si}_4\text{O}_8$. Secondly, terrestrial lavas contain water, which significantly depresses their liquidus compared to their lunar counterparts. Even if a terrestrial lava were to differentiate to a siliceous residual liquid, the temperature would be so low that $[]\text{Si}_4\text{O}_8$ would be below the detection limit (Fig. 9). The most siliceous terrestrial volcanic rocks (most favorable compositionally for $[]\text{Si}_4\text{O}_8$) also have the lowest liquidus temperatures (least favorable thermally for $[]\text{Si}_4\text{O}_8$) and *vice versa*. Plagioclases in terrestrial plutonic rocks should contain even less $[]\text{Si}_4\text{O}_8$ than those in the volcanic rocks, because they crystallize at even lower temperatures (Fig. 9). Applying these results to actual rocks, the detailed differences in $[]\text{Si}_4\text{O}_8$ zoning between samples can be used to compare the temperatures, nucleation histories, and liquid lines of descent of different magmas.

Because of the kinetic complications, care is needed when applying equilibrium phase diagrams to rapidly cooled samples. Once $[]\text{Si}_4\text{O}_8$ has been incorporated in a plagioclase crystal at high temperature, however, it is preserved. There is no evidence that the excess silica is lost, either through exsolution or diffusion, as the crystal cools to room temperature. For all but the most rapidly cooled samples, therefore, the amount of $[]\text{Si}_4\text{O}_8$ in the plagioclase as we measure it today is directly related to the condition of its formation.

If a magma is in equilibrium with cristobalite (or tridymite or quartz), the silica activity of the melt is buffered, and $[]\text{Si}_4\text{O}_8$ can be directly used as a geothermometer. This technique appears to be most promising as a means of comparing the solidus temperatures of lunar basalts. Measurement of the effect of albite substitution (determination of the An-Ab-Qtz ternary solvus) should enable this geothermometer to be quantified. Alternatively, for magmas with the same solidus temperatures, $[]\text{Si}_4\text{O}_8$ should allow measurement of the departure from equilibrium crystallization.

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