Homogeneous and heterogeneous polymorphic transformations in alkaline earth feldspars

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The displacive transformations in quartz, hexacelsian and the strontium equivalent of the latter, are homogeneous incipient transformations. These transformations are carried out mostly as a second (or higher) order reaction, and are finally completed abruptly as a first-order reaction which results from a sudden release of strain accumulated due to bond stretching. In such transformations the first-order mode of reaction seems to be eliminated to various extents by the introduction of impurities as solid solution to the structure. Such impurities promote heterogeneous transformations. The extent of sluggishness of displacive transformations and of stability relationship in alkaline earth feldspars is correlated with the various ionic sizes of barium, strontium and calcium. Displacive and diffusive transformations in alkali feldspars are also homogeneous incipient transformations, but due to the high mobility of the alkali ions, building up of strain is prevented and no abrupt change in symmetry occurs at the transformation. The hexacelsian $\rightleftharpoons$ celsian and monotropic transformations in $SrAl_2Si_2O_8$ and $CaAl_2Si_2O_8$ are heterogeneous incipient reconstructive transformations. Differences in melting temperatures reported in the past for $BaAl_2Si_2O_8$ may probably be correlated with the grain size, crystalline modification and extent of Al/Si order in the sample investigated.

1. Introduction
1.1. Polymorphism
Polymorphism is the ability of materials of a given chemical composition to be represented by two or more species. Understanding the reasons and mechanisms of polymorphic transformations provides important tools for mineralogists and geophysicists in their analyses of equilibrium and nonequilibrium conditions of minerals and rocks on the earth's surface as well as in deep seated formations. Material scientists use the same tools as a key for their elucidation of the modes of interaction and the crystallographic, microstructure, thermodynamic and kinetic properties of their substances. This information provides a guide for the improvement and control of phase stability of newly designed material systems.

Buerger's classification of polymorphic transformations [1, 2] is based on bonding energy and the nature of the structural change involved in the transformation. Classifications have also been based on kinetic considerations, and the descriptions sluggish [3] and rapid fitted quite well Buerger's main divisions of reconstructive and displacive transformations, respectively. A thermodynamic classification was also widely used [4]. Accordingly, in first-order transformation changes of the extensive properties (which are the first derivative functions of the Gibbs free energy) are discontinuous, and are gradual in higher orders.

Alkali feldspars are framework aluminosilicates of sodium and potassium ($NaAlSi_3O_8$ and $KAlSi_3O_8$ respectively). Alkali feldspar specialists have always been content with the simple division of polymorphic transformations into the two types, displacive and diffusive. According to this division the sanidine $\rightleftharpoons$ anorthoclase [5, 6], and monalbite

⇌ analbite [7, 8] transformations are displacive, and the orthoclase ⇌ microcline [9] and high albite ⇌ low albite [7] are disorder ⇌ order diffusive. The former disorder—order transformation had been predicted by Barth [10]. In alkaline earth feldspars ($CaAl_2Si_2O_8$, $SrAl_2Si_2O_8$ and $BaAl_2Si_2O_8$) on the other hand, polymorphic transformations are more numerous and more complicated. The problems involved with these polymorphic phase transformations are treated in the present study. This is partly done on the basis of the difficulties involved in defining the displacive transformation in quartz, as presented below.

1.2. The definition of the displacive transformation in quartz

There is still no clear definition of the displacive transformation in quartz. Buerger classifies the high—low transformation in quartz as basically second-order [11]. Majumdar et al. [12] consider the latter transformation as first-order, as it involves a volume change and a heat effect and it is instantaneous with a hysteresis loss of less than $1°C$. Buerger [13] suggests that there is a good rough correlation between the thermodynamic first-order transformation and the structural reconstructive transformation, and between the thermodynamic second-order transformation and the structural displacive and disordering transformations. He observes that many second-order displacive transformations terminate as first-order transformations. Roy [14] places the displacive transformation of quartz as mixed first- and second-orders. Heuer [15] equates first-order with heterogeneous (note also [16]), and higher orders of transformation with homogeneous transformations, commensurate with respective heterogeneous and homogeneous nucleating types, according to Christian [17]. Heuer suggests that the quartz displacive transformation is (heat-transport controlled) heterogeneous. A crystallographic approach to the problem is offered by Muller [18]. He suggests that the two components of the hexacelsian displacive transformation are not subgroups of each other, and therefore this transformation is first-order. If this model is followed, considering the fact that low quartz is a subgroup of high quartz [19], the displacive transformation in quartz is not first-order. Hence, after more than a hundred and forty years of research of polymorphism [10], there is still some

confusion as to the definition of the perhaps most classical polymorphic transformation.

2. Experimental procedure

Techniques for the preparation of glasses and glass-ceramics were described before [20]. Thermal expansion measurements of the glass-ceramic and rock specimens were obtained on a differential dilatometer with reference to the expansion of alumina. Heating and cooling rates were $400°C h^{-1}$, with readings taken at intervals of $10, 50$ or $100°C$.

3. Results
3.1. Displacive transformations in alkaline earth feldspars

The displacive transformation of low ⇌ high hexacelsian near $300°C$ [21] shows a discontinuous change in volume at the transformation (Fig. 1a). These low and high temperature modifications were defined by Takeuchi [22] as orthorhombic body centred and hexagonal respectively, a relationship that has been recently challenged by Muller [18]. Muller found that the supposed low and high modifications below and above $300°C$ were in fact $P6_3/mcm$ and $Immm$ respectively, and the stable stoichiometric hexacelsian at high temperatures (the equivalent of Takeuchi's high) is a third modification with the space group $P6/mmm$. It can be seen in Table I (DTA data) and Fig. 1 (dilatometric curves) that in Specimen 1 a discontinuous transformation occurred at about $275°C$, and in Specimens 2 and 3 (curves B and C respectively) the abrupt displacive transformation turned into gradual transformations without a discontinuous change in volume. Oehlschlegel et al. [23, 24] have noticed a decrease of transformation temperature due to a $Ba + 2Al = 2Si$ substitution in $BaAl_2Si_2O_8$. Hence, it appears that a transformation with first-order features in hexacelsian [21] is changed to a high-order transformation (perhaps second) due to impurities in the hexacelsian glass-ceramic (Table I). Of particular interest are the low amounts of impurities in Specimens 2 and 3 and their strong effects on the transformation. Presumably, these impurities are introduced into the hexacelsian structure; probably K substitutes for Ba and Zn substitutes for Al.

Displacive transformations similar to the one described in $BaAl_2Si_2O_8$ were described also in $SrAl_2Si_2O_8$ and $CaAl_2Si_2O_8$ hexagonal and pseudo-hexagonal polymorphs [25]. The rapid
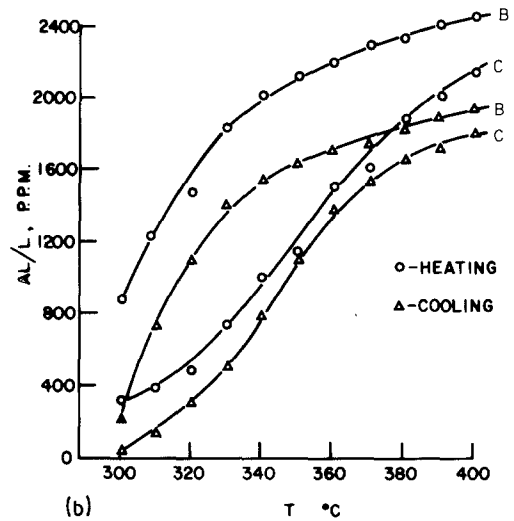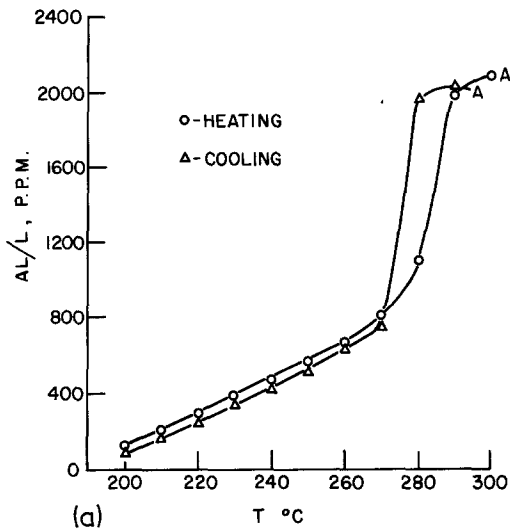
Figure 1 Expansion curves showing the effects of impurities on the displacive transformation of Hexacelsian in glass-ceramics. (a) A rapid transformation; (b) gradual transformations. Glass-ceramics A to C correspond to Nos. 1 to 3 in Table I.

TABLE I Selected compositions of alkaline earth feldspar glass-ceramics (in wt %).

	1	2	3	4	5
SiO_2	34.82			36.6	43.2
Al_2O_3	24.7			31.6	36.7
BaO	38.3			—	—
SrO	0.08			31.1	—
CaO	0.13			—	20.1
Na_2O	0.28				
K_2O	0.80		0.34		
FeO	0.22				
Fe_2O_3	0.48				
TiO_2	0.047				
ZnO	—	0.33			
MoO_3	—				1.0
$RhCl_3$				1.0	
DTA peak	2.75	330–340	310–350		

No. 1 is a chemical analysis. Nos. 2 and 3 are identical compositions to No. 1 with additional zinc and potassium oxides respectively, added as carbonates. No. 4 is a chemical analysis of a nominal stoichiometric $SrAl_2Si_2O_8$ glass, with an excess of $RhCl_3$. In No. 5 molybdenum oxide is added as an excess to a nominal composition, calculated from batch materials.

transformation in the strontium polymorphs is expected to have first-order features, and the sluggish transformation in the calcium polymorphs, of second or higher order (note discussion below).

3.2. Transformations in alkali feldspars

Not all displacive transformations show abrupt change in volume at the transformation tempera-

tures. Mackenzie [5] ran DTA on four natural anorthoclases (high temperature alkali feldspars) and did not find any definite evidence of discontinuity in the transformation range. Fig. 2 shows a dilatometric curve of a rock made essentially of natural anorthoclases ([26], No. 2 Table I). This curve does not show any discontinuity around $100°C$ where the displacive transformation from sanidine to anorthoclase is expected to occur [5]. The "collapse" [7] from the C2/m monoclinic
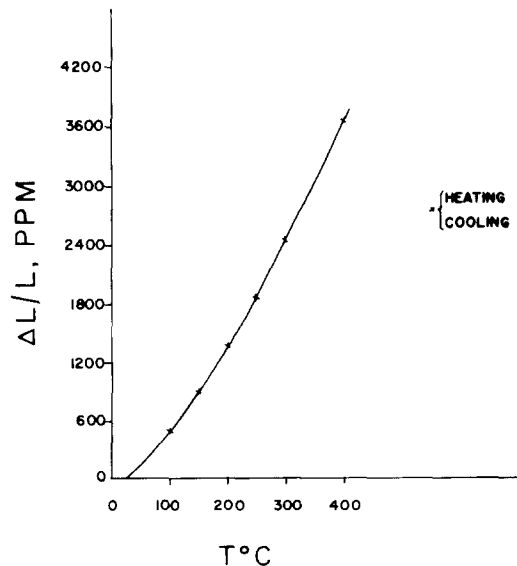

Figure 2 Expansion curve of a natural rock made essentially of anorthoclase (high temperature alkali feldspar) crystals.

(sanidine) to the $C\bar{1}$ triclinic feldspar (anorthoclase) on temperature reduction depends on the radius of the alkali cation, which decreases by either lowering the thermal motion [27] of potassium or by its substitution by sodium. Whereas Mackenzie [5] and Laves [7] suggest that the transformation temperature varies (inversely) with the crystallization temperature of the feldspar, Kroll and Bambauer [28] found that the transformation temperature is independent of the crystallization temperature, as long as a topologically monoclinic symmetry is possible. Waldbaum and Thompson ([29], Fig. 6) suggest that the transformation temperature of these symmetry changes is a time—temperature function (at a fixed pressure).

Polymorphic transformations involving plastic deformation due to internal strains that occur in metals (like the martensitic transformation) are not common in silicate crystals. It has however been suggested that the several gradual polymorphic transformations of alkali feldspar at room temperature [30] have resulted from such structural strain [8]. It should be added that the author tried to repeat the experiments reported in [8], and obtained different results when a different furnace was used in a different laboratory. The lack of reproducibility is assigned to the fact that conditions of chemical contamination in the two furnaces were different, and these may have been responsible for different behaviour of the feldspar, due to changes of nucleation conditions [31], or otherwise.

3.3. The monotropic transformations in $SrAl_2Si_2O_8$ and $CaAl_2Si_2O_8$

The hexagonal $SrAl_2Si_2O_8$ and $CaAl_2Si_2O_8$, (as opposed to $BaAl_2Si_2O_8$), and the orthorhombic $CaAl_2Si_2O_8$ do not have any fields of stability (at normal atmospheric pressure). Monotropic (i.e. irreversible) transformations of these structures to their respective stable monoclinic or triclinic modifications occur readily above $1000°$ C, dependent on nucleation conditions, promoted by the presence of impurities. Hexagonal $SrAl_2Si_2O_8$ glass-ceramics may be transformed to the stable modification even at $900°$ C when excess 2% WO_3 and MoO_3 are present in the original glass.

The melting point of a monoclinic strontium feldspar synthesised from glass of the stoichiometric composition was observed to be at $1665 \pm 3°$ C. The melting point of the same modification which was obtained from a glass-ceramic, which

had been nucleated by 1% $RhCl_3$ (Table I No. 4) to the high-symmetry form, and then transformed to the monoclinic symmetry, was observed to be at $1675 \pm 3°$ C. The feldspar that had been nucleated to hexacelsian and eventually transformed to a monoclinic structure was exposed to conditions more favourable to complete, uniform, and possibly more orderly (note below) crystallization than the feldspar that was devitrified to the monoclinic structure directly from the glass. This probably contributed to the former having a higher melting point.

The monotropic transformation of hexagonal $CaAl_2Si_2O_8$ to the triclinic modification following a heat treatment above $1250°$ C is shown in Fig. 3 (Table I No. 5).

4. Discussion
4.1. Homogeneous incipient transformations and deviating conditions

The gradual stretching of Si–O bonds with temperature prior to the transformation temperature of quartz ($573°$ C) that has been implied by crystallographic [32], volume [33] thermal [34], and by mechanical studies [35], is impressive. Also significant is the sharp inflection of the
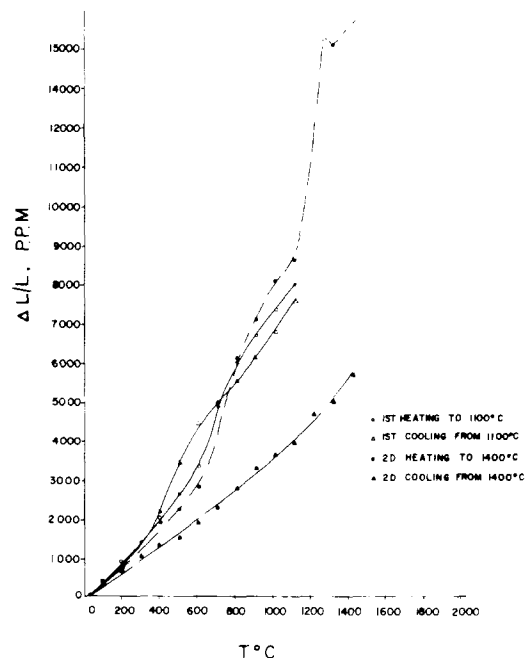

Figure 3 Expansion curves of hexagonal calcium and traces of triclinic feldspar glass-ceramics (first heating, first cooling and second heating) transformed to triclinic feldspar after being heated above $1250°$ C (second cooling). Chemical composition No. 4, Table I.

expansion curve at the transformation temperature [3]. All these features suggest that transformation in quartz is carried out mostly as a second- or higher-order reaction, and finally completed abruptly as a first-order reaction. This abrupt change results from a sudden release of the strain accumulated due to bond stretching. The transformation is homogeneous; it initiates everywhere within the transformed material, gradually at the beginning, and instantaneously at the end.

The displacive transformation in hexacelsian (and analogous $SrAl_2Si_2O_8$) is also homogeneous at the beginning and terminates as a first-order reaction. It is however, not clear from the specific heat data available [21] what is the extent of a second- or higher-order reaction prior to the discontinuous change. Possibly, it is not as extended as in quartz.

The sluggishness shown in Fig. 1b due to impurities in the hexacelsian structure indicates a complete alteration of the mechanism of transformation. No simultaneous stretching of bonds and no accumulation of strains occur, but rather, there is a heterogeneous gradual nucleation of various individual sites in the crystal that leads to transformation. Hence, this is considered to be a high-order (perhaps second) heterogeneous transformation. The displacive transformations in $SrAl_2Si_2O_8$ and $CaAl_2Si_2O_8$ [25] are analogous to the transformations in the uncontaminated (Fig. 1a) and contaminated (Fig. 1b) hexacelsian, respectively (note also effects of order—disorder below). Mobility of the alkaline earth ions in the hexagonal structures probably decreases with the increase of ionic radius from Ca to Ba. Consequently, strains have less relaxation, and a discontinuous change at the transformations is more pronounced in the strontium structure than in the calcium structure [25], and becomes a maximum in the barium structure (Fig. 1a).

McConnell [36] found that the disorder → order transformation in $KAlSi_3O_8$ closely associated with the development of transformation twins [37] (analogous to Dauphiné twins developed in low quartz following the displacive transformation) was connected with the growth of antisymmetrical domain nuclei. These domains were in fact regions of maximum distortion ([36], Fig. 4) which did not have discrete internal boundaries. They developed due to homogeneous fluctuations in the original (monoclinic) lattice during the symmetry reduction. The domain growth led to the development of transformation twinning. Electron optical studies [38] showed that the displacive transformations in anorthoclase was characterized by similar features to those of the disorder—order transformation in $KAlSi_3O_8$ [36]. Homogeneous distortion of the monoclinic binary $NaAlSi_3O_8$—$KAlSi_3O_8$ lattice was the incipience of symmetry transformation. McConnel [38] observed also growth of discrete nuclei of the developing triclinic phase. This was however associated with diffusion of the alkali ions and exsolution, and it is not clear to what extent the processes of exsolution and the transformation that followed were interdependent [38]. Regardless of the mechanisms of advanced stages of growth, homogeneous distortions were found by McConnell as the incipient conditions for both disorder → order and displacive transformations in alkali feldspars.

One faces here a problem of the definition of the incipient conditions of transformation. Should the strain domains resulted from bond distortions in the sluggish order—disorder transformation of $KAlSi_3O_8$, the displacive transformation in the $NaAlSi_3O_8$—$KAlSi_3O_8$ series, and the displacive transformations in quartz and hexacelsian, be regarded as heterogeneous, or rather, homogeneous (as suggested above). In other words, can these bond distortions be described by localized wave-like fluctuations characteristic of classical nucleation theory, or by infinitesimal wave-like fluctuations of the spinodal type which gradually grow in amplitude until a phase boundary is formed [39, 40]. The long dispute between the advocates of the crystallite and the random network glass structure models is an analogous problem. Both models are based on a continuous network and differ essentially in the degree of local atomic ordering, arguing whether the basic ordered units are 7, 11, 12 or 20 Å in size [41, 42].

Hence, fluctuations in strain domains of the above types in displacive and diffusive (order—disorder) transformations result in homogeneous transformations. They initiate gradual second-order (or higher) transformations, which may, or may not complete as second-order. Characteristically, these changes occur throughout the material and are infinitesimal.

Normally a final discontinuous change like that in quartz does not occur in alkali feldspars. Probably, the relatively high mobility of sodium in the structure helps to prevent building up of

strains. However, as impurities always occur in natural minerals, slight deviations are expected [28], partly due to heterogeneous nucleation. It was also shown [8] that probably under certain conditions of heat treatment and contaminated environment the expected homogeneous transformation from monoclinic to triclinic structure was suppressed when the material was removed from the furnace, and instead, a gradual heterogeneous transformation occurred at room temperature during an extended period of time of several months.

4.2. Heterogeneous incipient transformations

A kinetic study on the hexacelsian → celsian transformation [31] shows that it is a heterogeneously nucleated, thermally activated process. So are the monotropic transformations in $SrAl_2Si_2O_8$ and $CaAl_2Si_2O_8$.

The definition of the former transformation is however not trivial. The celsian → hexacelsian does not involve change in the coordination of Si and Al which form tetrahedra in both structures. The oxygen coordination of Ba, on the other hand, is changed from 9 [43] to 12 [22] respectively. This may be interpreted therefore as a change in secondary coordination, without change in the primary coordination. This transformation is quenchable and there is no crystallographic relationship between the two polymorphs. It may therefore be placed as reconstructive together with the quartz ⇌ tridymite and olivine ⇌ spinel transformations in Roy's syncretist classification ([14] Fig. 6). There is however an important deviation from this classification. The celsian ⇌ hexacelsian is a quenchable transformation but was shown to be in parts (if nucleation was provided) very rapid [31], and not necessarily very slow.

The hexacelsian and celsian modifications have different densities, 3.265 and 3.393 g cm^{-3} [24] respectively. This indicates that their transformation must involve some diffusion (displacement of the barium ion [31]). As a rule reconstructive transformations [14] are heterogeneous [17, 15] and understanding their kinetics seems to be more important than their thermodynamic characterization (note a different observation [14]). In these transformations research of the interrelationship between interface and diffusion controlled growth phenomena in general, and in silicate systems in particular, is far from being exhausted.

4.3. Order–disorder and stability in alkaline earth feldspars

Primitive triclinic calcium feldspar (anorthite), monoclinic barium feldspar (celsian) and also monoclinic strontium feldspar [44] have unit cell dimensions characterized by c repeats (of about 1.43 nm [45]) which doubles that of c of the alkali feldspars, as a result of Al_2Si_2 ordering [43]. That is, the structures of anorthite, celsian and the strontium monoclinic equivalent have ordered networks in which Si and Al tetrahedra (when equal in number) alternate. However, deviations from maximum order have been observed and variations in extents of disorder have been established [44, 46].

It is possible that the state of order–disorder in hexacelsian influenced by impurities in the structure, causes deviations in the displacive transformation. Accordingly, the nature of the new metastable polymorph discovered by Muller [18] could also be dependent on the degree of order–disorder. Muller speculated that "the temperature of the transition P6/mcm ⇌ Immm depends apparently on the chemical composition, but could also be influenced by the cooling history". The degree of Al/Si order in feldspars is highly dependent on their cooling history [10, 45], and so is the transformation temperature [29].

Differences for melting temperatures of $BaAl_2Si_2O_8$ obtained by various investigators including 1715° C [21], 1740° C [42] and 1760° C [48], were probably related to differences in grain size of samples and the actual phase investigated. An additional contributor to these differences could well be the degree of Al/Si tetrahedral disorder in the celsian and hexagonal modifications and their strontium and calcium analogues. A high degree of order in the low-symmetry alkaline earth feldspars may raise the melting temperature of the mineral, and a high degree of disorder in the high-symmetry alkaline earth feldspars would have the same effect.

There is a correlation between the extreme hexacelsian stability field at high temperatures and the high general persistency of hexacelsian as metastable at low temperatures, and the lack of stability fields for the high symmetry forms of $SrAl_2Si_2O_8$ and $CaAl_2Si_2O_8$ at high temperatures, and their general low persistency as metas-

table at low temperatures. The refractoriness of the stable modifications and persistence of the metastable phases generally increase with the ionic size of the alkaline earth.

4.4. Materials engineering

The gradual displacive transformations of hexacelsain glass-ceramics (Fig. 1b) is of interest to the material engineer, as a technique by which high strains accumulated in the material during thermal cycling may be avoided.

Acknowledgements

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