

# Mechanochemical interaction of Ca silicate and aluminosilicate minerals with carbon dioxide

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Processes induced by mechanical activation (MA) in a planetary ball mill of natural diopside  $\text{CaMgSi}_2\text{O}_6$  and plagioclase  $(\text{CaAl}_2\text{Si}_2\text{O}_8)_{0.745} \cdot (2\text{NaAlSi}_3\text{O}_8)_{0.209} \cdot (2\text{KAlSi}_3\text{O}_8)_{0.046}$  in  $\text{CO}_2$  atmosphere have been studied. Plagioclase like diopside consumes  $\text{CO}_2$  during MA in the form of distorted carbonate groups resulting in appearance of the double IR absorption band in  $1400\text{--}1600\text{ cm}^{-1}$  region corresponding to the stretching vibrations of  $\text{CO}_3^{2-}$  group. The degree of spitting of the double carbonate band for plagioclase is markedly higher than that for diopside indicating increased distortion of  $\text{CO}_3^{2-}$  group in the mechanically activated plagioclase. According to the XRD data after 25 min of MA the diopside and plagioclase samples are almost totally amorphous. The carbonization degree of the plagioclase is lower than that of diopside after MA at the same conditions. The differences in the mechanically induced  $\text{CO}_2$  sorption ability by silicates can be explained on the basis of simple thermodynamic considerations involving standard Gibbs free energies of reactions of the crystalline minerals with carbon dioxide producing crystalline carbonates, silica and alumina. The results on thermal relaxation of the activated samples have been reported. © 2004 Kluwer Academic Publishers

## 1. Introduction

In our previous work [1, 2] we have revealed that prolonged dry grinding in air of Ca- and/or Mg-containing silicates such as diopside  $\text{CaMgSi}_2\text{O}_6$ , enstatite  $\text{MgSiO}_3$ , åkermanite  $\text{Ca}_2\text{MgSi}_2\text{O}_7$ , and wollastonite  $\text{CaSiO}_3$  alongside with amorphization results in considerable sorption of atmospheric carbon dioxide by the ground minerals. Diopside in the course of mechanical activation (MA) in  $\text{CO}_2$  atmosphere consumes carbon dioxide in amounts comparable with the Ca content in the mineral and even more [3] and may contain, in the limit, up to 20–25 wt%  $\text{CO}_2$ . Considering such a high  $\text{CO}_2$  content in the ground mineral it is reasonable to assume that crystalline carbonates may have been mechanochemically formed. However the XRD

patterns of the mechanically activated silicates do not show even the slightest peaks of calcite or other crystalline carbonates and are completely amorphous. We do not suggest the formation of amorphous calcium carbonate in the course of MA as well because according to the literature data  $\text{CaCO}_3(\text{am})$  is unstable and readily transforms to calcite [4, 5]. In our experiments we did not observe the formation of crystalline carbonates in mechanically activated silicates during their storage in a desiccator for 3 years.

According to the IR spectroscopic data carbon dioxide is present in the mechanically activated minerals in similar form as in silicate glasses containing dissolved  $\text{CO}_2$  that is in the form of distorted carbonate groups

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incorporated in disordered silicate matrix presumably associated with divalent metals [1–3].

It is known [6] that fine grinding of silicates leads to the formation of a surface phase distinct in structure from the bulk crystal. Composition of a newly formed surface phase also may differ from the bulk material due to the sorption of gas molecules from the environment. The formation of a surface phase is presumed to result from melting of crystalline mineral due to the local high-temperature heating up at small contact spots of the colliding particles and/or from plastic deformations [6–9]. It seems likely that the prolonged fine grinding of the calcium containing silicates brings into existence a special active state of the disordered silicate matrix and extensive consumption of CO<sub>2</sub> by the mechanically activated mineral has become possible. As a result a substance resembling the CO<sub>2</sub> containing silicate glasses quenched from melts [10, 11] is formed. Remarkable is the fact that similar state of CO<sub>2</sub>-bearing disordered silicate matrix is reached by such different ways as the carbon dioxide sorption during fine grinding of mineral at ambient conditions on the one hand and the dissolution of CO<sub>2</sub> in silicate melts at high temperatures and pressures relevant to the terrestrial magma on the other.

We assumed that the ability to extensive sorption of CO<sub>2</sub> during grinding is not the characteristic feature only of examined Ca- and Mg-containing minerals and involved other classes of silicates in the research. Titanite CaTiSiO<sub>5</sub>, being calcium titanosilicate, readily reacts with CO<sub>2</sub> during grinding, similar to diopside [12]. It was found that in a row enstatite MgSiO<sub>3</sub>—diopside CaMgSi<sub>2</sub>O<sub>6</sub>—titanite CaTiSiO<sub>5</sub>—åkermanite Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>—wollastonite CaSiO<sub>3</sub> there is a correlation between the carbonization degree of the ground minerals and: (1) Gibbs free energies of reactions of crystalline minerals with carbon dioxide; and (2) the CaO content in the chemical formula of mineral [12].

This study is a part of our work on mechanical activation of silicates with different compositions and structures. One of our purposes is to compare the processes occurring in the course of MA of plagioclase as Ca-containing aluminosilicate with those of previously studied Ca-containing silicate diopside.

Plagioclases (Ca-Na feldspars) are wide spread aluminosilicates. Mechanically activated plagioclases as well as diopside are used in ceramic and building materials technologies [13, 14]. Plagioclases form a discontinuous solid solutions from anorthite CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> to albite NaAlSi<sub>3</sub>O<sub>8</sub> by substitution of Ca and Al for Na and Si [15]. They often contain microcline KAlSi<sub>3</sub>O<sub>8</sub>. It should be noted that among Ca-Na feldspars pure endmembers are absent. The structure of plagioclase (triclinic) is based on three-dimensional framework of (Al,Si)O<sub>4</sub> tetrahedra. Each oxygen atom belongs to two tetrahedra and each tetrahedron is a member of four-

member ring. The rings are linked together to form a three-dimensional structure where Ca, Na or K fill up the interstices between rings and are linked to oxygen atoms.

Diopside CaMgSi<sub>2</sub>O<sub>6</sub> belongs to the pyroxene mineral group and its structure possess monoclinic symmetry [15]. Structure of diopside is based on single (SiO<sub>3</sub>)<sub>n</sub> chain which is formed by sharing two out of four corners of SiO<sub>4</sub> tetrahedra. The chains are cross-linked by divalent metal atoms. Calcium and magnesium atoms occupy eightfold and sixfold coordination positions, respectively.

The goal of this study is to elucidate the influence of alkali metals and aluminium present in plagioclase on the mechanochemical interaction of the mineral with carbon dioxide. Another our purpose is to verify the correlation between the degree of mechanically induced carbonization of silicate minerals and Gibbs free energies of reactions of the appropriate crystalline minerals with carbon dioxide.

## 2. Experimental

Both diopside and plagioclase samples (fractions-200+125 μm) were from Kola Peninsula, Russia. The diopside sample was the same as in our previous study [3]. It contained less than 1% of carbonates and micas as admixtures. The plagioclase sample was not as pure as diopside. Optical microscopy analysis revealed that the sample contained 3–5% of secondary minerals such as epidote and micas. These minerals may result from the high-temperature geochemical alteration of plagioclase in contact with water. The presence of micas in the plagioclase is confirmed by IR spectroscopic data (see below). The compositions of the initial minerals according to chemical and atomic absorption spectroscopy analyses are given in Table I. The chemical formula of the plagioclase can be approximately expressed as (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>)<sub>0.745</sub> · (2NaAlSi<sub>3</sub>O<sub>8</sub>)<sub>0.209</sub> · (2KAlSi<sub>3</sub>O<sub>8</sub>)<sub>0.046</sub> or (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>)<sub>0.593</sub> · (NaAlSi<sub>3</sub>O<sub>8</sub>)<sub>0.332</sub> · (KAlSi<sub>3</sub>O<sub>8</sub>)<sub>0.075</sub>. According to anorthite/albite percentage the plagioclase sample can be classified as labradorite [15].

MA of the samples was carried out in a planetary mill AGO-2 [9] at centrifugal acceleration of 60 g. Steel balls 5 mm in diameter were used as milling bodies. The ball-to sample mass ratio was 20. Water cooling of drum was used to prevent heating during activation. Before beginning the experiments balls and sample were loaded into drum. The carbon dioxide was “poured in” drum for several minutes at ambient pressure from a tube connected to a gas cylinder to replace air and then drum was hermetically closed. After each 5 min of MA drums were taken from milling chamber and refilled with CO<sub>2</sub> using the procedure described above.

TABLE I Chemical compositions of the initial diopside and plagioclase samples (wt%)

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	FeO	Fe <sub>2</sub> O <sub>3</sub>	MgO	TiO <sub>2</sub>
Diopside	49.70 ± 0.30	1.34 ± 0.05	24.50 ± 0.15	0.43 ± 0.05	0.19 ± 0.02	2.88 ± 0.05	–	16.10 ± 0.10	0.48 ± 0.05
Plagioclase	50.50 ± 0.30	28.30 ± 0.15	11.60 ± 0.10	3.60 ± 0.05	1.20 ± 0.05	–	0.74 ± 0.05	0.28 ± 0.02	0.07 ± 0.02

IR spectra were recorded in KBr pellets using a UR-20 spectrometer. DRON-2 diffractometer (Cu  $K_{\alpha}$  radiation) was used to obtain XRD patterns of the samples. Thermal analysis was carried out using NTR-70 and PRT-1000 devices with Pt-Pt/Rh thermocouple. Sample heating rate was  $10 \text{ K}\cdot\text{min}^{-1}$ , the annealed  $\text{Al}_2\text{O}_3$  was used as reference.

The  $\text{CO}_2$  content in the samples was determined by volumetric technique with a fast-response gas analyser AN-7529 using preliminary thermal decomposition of the sample.

### 3. Results and discussion

#### 3.1. IR spectroscopic examination

The IR spectra of the initial diopside and plagioclase minerals and the samples after MA for 10 and 25 min in  $\text{CO}_2$  atmosphere are shown in Figs 1 and 2. The bands at  $400\text{--}550 \text{ cm}^{-1}$  and at  $850\text{--}1200 \text{ cm}^{-1}$  in the spectra of both initial samples can be attributed to O—Si—O bending and antisymmetric Si—O—Si stretching vibrations, respectively [16]. The sharp bands at  $850\text{--}1200 \text{ cm}^{-1}$  in the IR spectrum of initial diopside (Fig. 1a) belong to the characteristic “diopside type” bands [17, 18]. The broadening of the absorption band in the same region in the spectrum of initial plagioclase (Fig. 2a) apparently results from Al—Si disorder [16, 19]. MA of both minerals leads to broadening and merging of the absorption bands at  $400\text{--}1200 \text{ cm}^{-1}$  indicating considerable distortions in the crystal structures and amorphization.

The presence of micas as impurities in the initial plagioclase results in appearance of two small sharp bands at  $3490$  and  $3640 \text{ cm}^{-1}$  (not shown) corresponding to hydroxyl stretching vibrations. The absence of band at  $1640 \text{ cm}^{-1}$  in the spectrum of the initial plagioclase (Fig. 2a) indicates that hydroxyls are present only as

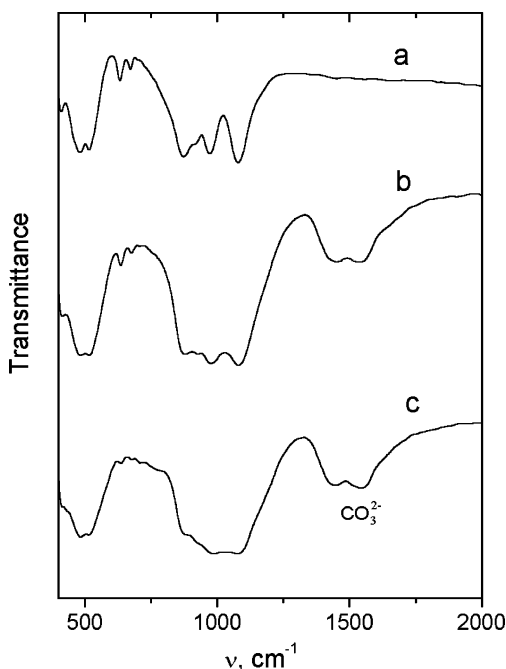


Figure 1 IR spectra of diopside: a—initial sample; b and c—after mechanical activation in AGO-2 in  $\text{CO}_2$  atmosphere for 10 and 25 min, respectively.

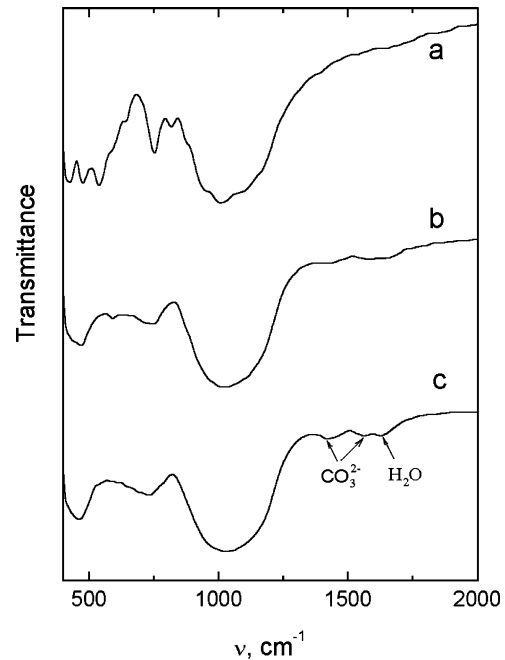


Figure 2 IR spectra of plagioclase: a—initial sample; b and c—after mechanical activation in AGO-2 in  $\text{CO}_2$  atmosphere for 10 and 25 min, respectively.

isolated OH-groups in micas structure. In the course of MA the bands at  $3490$  and  $3640 \text{ cm}^{-1}$  gradually transform to one broad peak at  $3500 \text{ cm}^{-1}$  (not shown). In addition the peak at  $1640 \text{ cm}^{-1}$  arises (Fig 2b and c). It is known [20] that amorphization of micas in the course of MA leads to the transformation of isolated structural hydroxyls to molecular water that corresponds to the appearance of band at  $1640 \text{ cm}^{-1}$  due to OH-bending vibrations of  $\text{H}_2\text{O}$  molecules. It is possible as well that atmospheric moisture is adsorbed onto the surface of the ground samples after exposure in air.

MA of diopside in  $\text{CO}_2$  atmosphere, in agreement with earlier work [1, 3], leads to the appearance of the strong double band with maxima  $1445$  and  $1540 \text{ cm}^{-1}$  corresponding to  $\nu_3$  antisymmetric stretching vibrations of  $\text{CO}_3^{2-}$  group (Fig. 1b and c). For the mechanically activated plagioclase the changes in the  $1400\text{--}1600 \text{ cm}^{-1}$  range (Fig. 2b and c) are not so pronounced as for diopside. This observation correlates well with the amounts of carbon dioxide consumed by both the ground diopside and plagioclase samples in the course of MA (Table II). Still from Fig. 2c it is clearly seen that the IR spectrum of the plagioclase after MA for 25 min in  $\text{CO}_2$  atmosphere exhibits double absorption band with maxima at  $1410$  and  $1580 \text{ cm}^{-1}$ , which can be also attributed to the stretching vibrations of carbonate group. This double band is

TABLE II Carbon dioxide content of the initial and mechanically activated (in  $\text{CO}_2$  atmosphere) diopside and plagioclase samples

Sample	MA (min)	$\text{CO}_2$ (wt%)
Diopside	—	$0.30 \pm 0.03$
	10	$4.1 \pm 0.1$
	25	$6.4 \pm 0.2$
Plagioclase	—	$0.16 \pm 0.02$
	10	$1.55 \pm 0.05$
	25	$2.08 \pm 0.05$

partially overlapped with OH-bending vibrations band ( $1640\text{ cm}^{-1}$ ).

The intensity of the double carbonate band in  $1400\text{--}1600\text{ cm}^{-1}$  range in IR spectra of the mechanically activated plagioclase (Fig. 2b and c) is lower and its broadness is markedly larger than that in case of diopside (Fig. 1b and c). It is clearly seen that  $\nu_3$  band of  $\text{CO}_3^{2-}$  group in the spectra of mechanically activated plagioclase quite differ in splitting from that of Ca-containing silicates such as diopside as well as åkermanite, wollastonite [2] and titanite [12]. It should be noted that the degree of spitting of  $\nu_3$  mode of carbonate ions provides information on  $\text{CO}_3^{2-}$  group local environment. For mechanically activated diopside as well as for the other Ca and/or Mg silicates studied earlier [2, 12] the observed splitting is about  $100\text{ cm}^{-1}$ . In comparison for the plagioclase sample after MA in  $\text{CO}_2$  atmosphere this value is  $\sim 170\text{ cm}^{-1}$  (Fig. 2c). According to [21], carbonate containing aluminosilicate glass of similar composition quenched from  $\text{CO}_2$ -saturated albite-anorthite melt exhibited analogous IR absorption band in the same region with the similar degree of splitting ( $\sim 200\text{ cm}^{-1}$ ). Apparently carbon dioxide in the mechanically activated plagioclase is present in the form of distorted carbonate groups but because of the different local environment the degree of distortion of  $\text{CO}_3^{2-}$  anion is considerably larger than that for the previously studied Ca and/or Mg silicate minerals. It is remarkable that our results resembles suggestions of Fine and Stolper [11] who reported that  $\nu_3$  bands of  $\text{CO}_3^{2-}$  groups in a wide range of  $\text{CO}_2$ -bearing glasses with dominantly divalent network modifying cations, including basaltic glasses, glasses in the system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ , diopside and åkermanite glasses were split almost identically, but quite differently from the Na-bearing aluminosilicate glasses. However, it needs further examinations to decide how the interaction between aluminium, divalent (Ca, Mg) and alkali (Na, K) metals influences the increased distortion of carbonate groups in the mechanically activated aluminosilicates.

### 3.2. XRD measurements

The XRD patterns of the initial and mechanically activated minerals are shown in Figs 3 and 4. In agreement with the IR spectroscopy data MA of both minerals results in dramatic decreasing of intensities and broadening of the main peaks. Most of the lower intensity peaks in the XRD patterns of initial samples after 10 min of MA practically disappeared. After 25 min of MA both samples were almost totally amorphous (Figs 3c and 4c). From the data presented in Figs 3 and 4 it is seen that the crystal lattice of the plagioclase is slightly less stable with respect to MA in comparison to that of the diopside.

### 3.3. Thermodynamic considerations

In earlier work [12] using thermodynamic approach we have revealed approximately a linear correlation between the  $\text{CO}_2$  content in the finely ground Ca(Mg)-

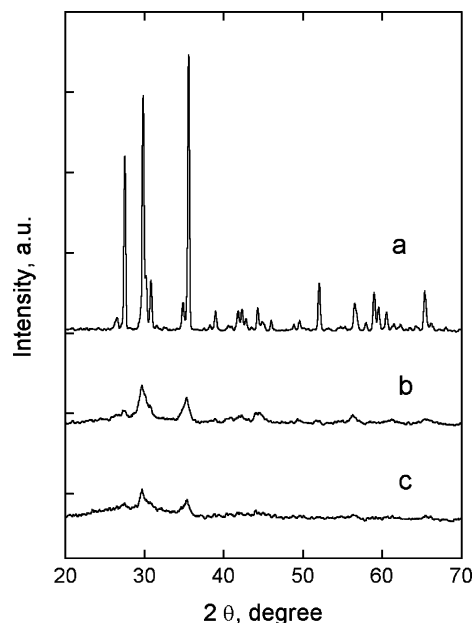


Figure 3 XRD patterns of diopside: a–initial sample; b and c–after mechanical activation in AGO-2 in  $\text{CO}_2$  atmosphere for 10 and 25 min, respectively.

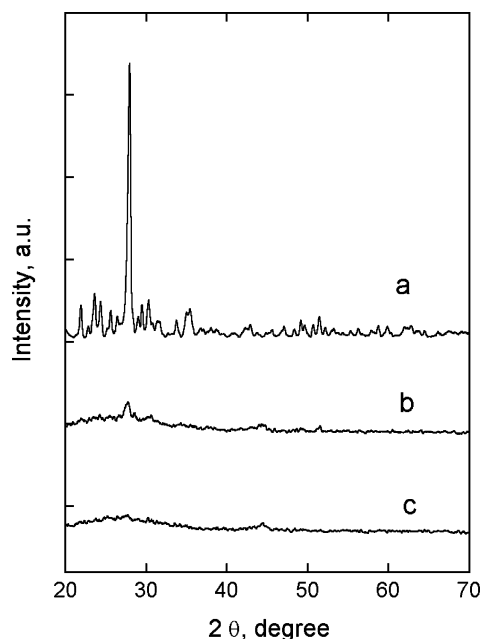
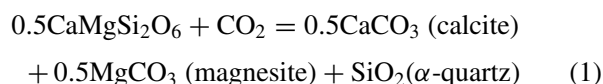


Figure 4 XRD patterns of plagioclase: a–initial sample; b and c–after mechanical activation in AGO-2 in  $\text{CO}_2$  atmosphere for 10 and 25 min, respectively.

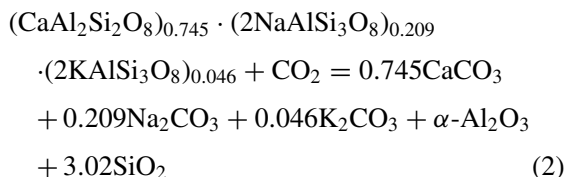
bearing silicate minerals and standard Gibbs free energy of reactions of crystalline minerals with carbon dioxide producing crystalline carbonate(s) and silica ( $\Delta_r G^\circ$ ). For diopside this reaction referred to 1 mole of  $\text{CO}_2$  may be written in the form:



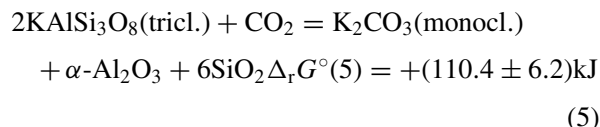
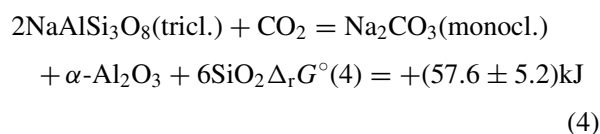
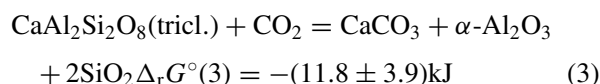
Standard Gibbs free energy for this reaction ( $P^\circ = 0.1\text{ MPa}$ ,  $T = 298.15\text{ K}$ ) calculated using reference data [22] is  $\Delta_r G^\circ(1) = -(18.3 \pm 5.4)\text{ kJ}$ . As was already mentioned no carbonates as individual solid

phase were detected in the mechanically activated silicates even if they consumed CO<sub>2</sub> in amounts comparable with the Ca content in the minerals. So, the reaction (1) can be regarded only as an approximation. Nevertheless this approach proved to be useful [12].

In this study the same approach has been used in respect of mechanically activated plagioclase. For the plagioclase sample the similar reaction may be written as:



Unfortunately, we could not find in literature the standard Gibbs free energies of formation of plagioclases containing calcium, sodium, and potassium simultaneously, which is necessary for calculation of the  $\Delta_r G^\circ$  value of reaction (2). However using reference data [22] it is possible to calculate the  $\Delta_r G^\circ$  values of the corresponding reactions for pure anorthite and albite, as plagioclase endmembers, and for KAlSi<sub>3</sub>O<sub>8</sub> component:



For anorthite the  $\Delta_r G^\circ$  value of the reaction (3) is negative and within the uncertainty limits is equal to the corresponding value for pure magnesium silicate enstatite MgSiO<sub>3</sub> [12]. For albite and especially for microcline the  $\Delta_r G^\circ$  values of the reactions (4) and (5) are highly positive. So, the reactions (4) and (5) are thermodynamically unfavorable.

As is mentioned above the major components of natural plagioclase are albite and anorthite. For simplicity the microcline component can be neglected. Taking into account the  $\Delta_r G^\circ$  values of reactions (3) and (4), one would expect that plagioclases with the anorthite component predominant will display a certain ability to consume carbon dioxide during grinding. In line with this approach the degree of carbonization of the ground plagioclase will noticeably diminish as the albite content increases. However according to our preliminary results the mechanically induced CO<sub>2</sub> sorption ability of albite-rich plagioclase involving about 80 mol% of NaAlSi<sub>3</sub>O<sub>8</sub> and 20 mol% of CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> is practically the same as that of the plagioclase sample studied here (~60 mol% of CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>). The following explanation of this disagreement seems possible. The process

of CO<sub>2</sub> sorption by silicate in the course of MA resulting in the formation of the carbonate containing amorphous substance can be conditionally presented (only for better understanding of the observed disagreement) as a consequence of 3 stages:

- (1) interaction between silicate mineral and CO<sub>2</sub> producing crystalline carbonate(s), SiO<sub>2</sub> (or SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub>);
- (2) amorphization of the SiO<sub>2</sub> (or SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub>) component;
- (3) "dissolution" of the newly formed carbonate(s) in the solid amorphous silicate (aluminosilicate) matrix.

Thus, the Gibbs free energy change of the resulting process ( $\Delta G^\Sigma$ ) consists of three terms:

$$\Delta G^\Sigma = \Delta G^{(1)} + \Delta G^{(2)} + \Delta G^{(3)}, \quad (6)$$

where  $\Delta G^{(i)}$  is the Gibbs free energy change for the *i*-th stage. The first term on the right-hand side of Equation 6 is equal to  $\Delta_r G^\circ$  value for the conversion of crystalline silicate to crystalline carbonate(s) (e.g., reactions (1)–(5)). The second term ( $\Delta G^{(2)}$ ) is independent of the carbonate forming cations, so its contribution to  $\Delta G^\Sigma$  is approximately the same for the studied silicates. There appears to be small difference in the third term ( $\Delta G^{(3)}$ ) for CaCO<sub>3</sub> and MgCO<sub>3</sub> due to the similarity of calcium and magnesium properties. Hence the difference in  $\Delta G^\Sigma$  for Ca and/or Mg silicates will be determined by the difference in  $\Delta_r G^\circ$  values which can be calculated using reference data.

In case of the Na-Ca aluminosilicates the situation is dissimilar. The difference in  $\Delta_r G^\circ$  values for Na<sub>2</sub>CO<sub>3</sub> and CaCO<sub>3</sub> is likely to be more pronounced. We infer that for sodium carbonate the third stage thermodynamically is markedly more favorable than that for calcium carbonate. Thus, the negative value of  $\Delta_r G^\circ$  for sodium carbonate would compensate the positive value of  $\Delta_r G^\circ$  which is equal to  $\Delta_r G^\circ(4) = +(57.6 \pm 5.2)$  kJ. The resulting values of  $\Delta G^\Sigma$  for pure sodium and pure calcium aluminosilicates would be rather close. Then the carbonization degree of plagioclases during MA would not be strongly dependent on albite/anorthite ratio. Considering the analogy between the studied samples and CO<sub>2</sub>-bearing aluminosilicate glasses this is in agreement with the fact that solubility of carbon dioxide changes only to a small extent from pure albite to pure anorthite melts and is about 2 wt% at 1450–1570°C and *P* = 3 GPa [21].

### 3.4. Speciation of CO<sub>2</sub> in the mechanically activated silicates

It should be noted that the CO<sub>2</sub>-bearing sodium aluminosilicate glasses studied by Brey [21] and by Fine and Stolper [10] contained both dissolved molecular CO<sub>2</sub> and carbonate ions (in contrast with Ca, Mg-bearing silicate glasses in which CO<sub>2</sub> dissolved only as carbonate [11]). According to Fine and Stolper [10] molecular form of CO<sub>2</sub> in silicate melts is structurally bound molecular CO<sub>2</sub>, that is molecular CO<sub>2</sub> homogeneously

dissolved at molecular scale (IR absorption band at  $\sim 2352\text{ cm}^{-1}$ ). Taking into account the analogy between  $\text{CO}_2$ -bearing silicate glasses quenched from melts and the silicates containing carbon dioxide consumed in the process of grinding we might expect that our mechanically activated plagioclase samples also contain molecular  $\text{CO}_2$ . However we could not detect molecular  $\text{CO}_2$  in none of our ground samples at all although we have examined the aluminosilicate samples with the essentially different contents of albite and anorthite and even the almost pure albite. This may confirm the suggestion of Brey [21] that the molecular  $\text{CO}_2$  in glasses is a quenching phenomenon, in other words, it appears in glasses only during quenching of melt.

### 3.5. DTA and TG examination

DTA curves of diopside and plagioclase samples after 25 min of MA in  $\text{CO}_2$  atmosphere (not shown) exhibit the pronounced exothermic crystallization peaks at  $750$  and  $910^\circ\text{C}$ , respectively. Removal of carbonate from the mechanically activated diopside as indicated by TG results and IR spectroscopic measurements (not shown) occurs in  $700\text{--}850^\circ\text{C}$  region, so the endothermic peak of carbonate decomposition is overlapped with exothermic peak of the mineral crystallization. The mechanically activated plagioclase releases  $\text{CO}_2$  in  $500\text{--}650^\circ\text{C}$  region indicating lower stability of the carbonate complexes in comparison to those in the diopside samples.

### 4. Conclusions

(1) Plagioclase ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) $_{0.745}$ ·( $2\text{NaAlSi}_3\text{O}_8$ ) $_{0.209}$ ·( $2\text{KAlSi}_3\text{O}_8$ ) $_{0.046}$  (natural aluminosilicate) like diopside in the course of MA consumes  $\text{CO}_2$  in the form of distorted carbonate groups resulting in appearance of the double IR carbonate absorption band at  $1400\text{--}1600\text{ cm}^{-1}$ . The degree of spitting of the double carbonate band for plagioclase ( $\sim 170\text{ cm}^{-1}$ ) is markedly higher than that for diopside and the previously studied silicates ( $\sim 100\text{ cm}^{-1}$ ) indicating increased distortion of  $\text{CO}_3^{2-}$  group in the mechanically activated plagioclase. In this respect the similarity has been observed with  $\text{CO}_2$ -bearing silicate and aluminosilicate glasses.

(2) The carbonization degree of the plagioclase after MA in planetary ball mill in  $\text{CO}_2$  atmosphere is lower than that for diopside after MA at the same conditions. According to preliminary results the mechanically induced  $\text{CO}_2$  sorption ability of plagioclases only slightly depends on albite/anorthite ratio. The differences in the  $\text{CO}_2$  sorption ability by silicates and aluminosilicates in the course of MA can be explained on the basis of simple thermodynamic considerations involving standard Gibbs free energies of reactions of the crystalline minerals with carbon dioxide producing crystalline carbonates, silica and alumina.

(3) After 25 min of MA the diopside and plagioclase samples are almost totally amorphous. The stability of crystal lattice of the plagioclase during of MA in planetary ball mill in  $\text{CO}_2$  atmosphere is slightly less than in case of diopside.

(4) According to thermal analysis data the mechanically activated diopside and plagioclase samples release  $\text{CO}_2$  in  $700\text{--}850^\circ\text{C}$  and  $500\text{--}650^\circ\text{C}$  ranges, respectively, indicating lower stability of the carbonate complexes in the latter.

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