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Computer simulation of feldspar structures

J. PURTON
Department of Chemistry, University of Keele, Keele, Staffordshire ST5 5BG, United Kingdom
C.R.A. CATLOW
Davy Faraday Research Laboratory, The Royal Institution, 21 Albemarle Street, London W1X 4BS, United Kingdom

ABSTRACT

Lattice-energy minimization calculations have been performed for the feldspars low albite, maximum microcline, and anorthite using an ionic Born-model potential. Analysis of earlier work shows that, although the bond lengths are simulated with reasonable accuracy using a two-body rigid-ion model, the bond angles display significant differences from the experimental results. The inclusion of three-body terms and polarization effects overcomes these problems. The T-O-T bond angles are particularly sensitive to the nature of the short-range cation-O potential.

INTRODUCTION

Feldspars are important rock-forming minerals present in a wide variety of igneous, metamorphic, and sedimentary rocks. Their ubiquitous nature has led to considerable research on their structural, physical, and chemical properties (see, for example Smith, 1974a, 1974b; Ribbe, 1983). Despite the recent interest in computer simulation of minerals and other inorganic compounds, there has only been a limited amount of work on feldspars. The most basic requirement of any simulation is the ability to reproduce the crystal structure. Thus the present paper reports a simulation study of feldspar structures as a precursor to investigating other physical and chemical properties (e.g., defects, hydrolysis, and Si-Al ordering). Our methodology is based on the use of three-body shell model potentials, which are employed in energy minimization calculations. We pay special attention to the contrast between our results and those of earlier studies (Post and Burnham, 1987) in which only two-body models were employed.

METHOD

Our techniques are based on lattice-energy minimization. We employ the THBREL code, which calculates lattice energies by a direct summation of two- and three-body short-range terms, and an Ewald summation of the Coulombic interactions. The lattice-energy calculations are coupled with a Newton-Raphson minimization procedure. The observed crystal structures used as the starting point for the calculations are those of Harlow and Brown (1980), Brown and Bailey (1964), and Wainwright and Starkey (1971) for low albite, maximum microcline, and anorthite, respectively. The Al atoms were assumed to be fully ordered into the T1o site of albite and microcline and the T1(0z00), T1(0zi0), T1(m000), T1(m0i0), T2(0000), T2(mz00), and T2(mzi0) sites of anorthite. The relaxation was carried out to zero pressure, allowing both atom coordinates and cell dimensions to vary simultaneously. Calculations were performed with two types of potential for all of the minerals. The first was a rigid-ion two-body model (2BRI) in which the electrostatic forces are counterbalanced by short-range repulsive forces. The electrostatic or Coulomb (U_c) energy is given by

$$U_c = \frac{1}{2} \sum_{i}^{\text{one cell}} \sum_{j \neq i}^{\text{all cells}} q_i q_j r_{ij}^{-1} \tag{1}$$

where q is the formal charge and r_{ij} the interionic dis-

TABLE 1. Short-range potentials

Interaction	A (eV)	ρ (Å)	C (eV Å^6)	Method	Reference
Two-body rigid-ion model					
Si^{4+}-O^{2-}	3711.976	0.2428	0.0	MEG	a
Al^{3+}-O^{2-}	3445.302	0.2461	0.0	MEG	a
O^{2-}-O^{2-}	3016.013	0.2876	0.0	MEG	a
Na^{+}-O^{2-}	5836.814	0.2387	0.0	MEG	a
K^{+}-O^{2-}	65269.710	0.2134	0.0	MEG	a
Ca^{2+}-O^{2-}	6958.232	0.2516	0.0	MEG	a
Three-body shell model					
Interaction	A (eV)	ρ (Å)	C (eV Å^6)	Method	Reference
Si^{4+}-O^{2-}	1283.907	0.32052	10.66158	EMP	b
Al^{3+}-O^{2-}	1460.300	0.29912	0.0	EMP	c
O^{2-}-O^{2-}	22764.000	0.149	27.88	HF	d
Na^{+}-O^{2-}(1)	1266.840	0.3065	0.0	EMP	e
Na^{+}-O^{2-}(2)	5836.814	0.2387	0.0	MEG	a
K^{+}-O^{2-}(1)	1000.300	0.36198	0.0	EMP	f
K^{+}-O^{2-}(2)	65269.710	0.2134	0.0	MEG	a
Ca^{2+}-O^{2-}(1)	1227.700	0.3372	0.0	EMP	g
Ca^{2+}-O^{2-}(2)	6958.232	0.2516	0.0	MEG	a
Harmonic force constant for O core shell (k_s)			74.92 eV Å^{-2}		
O core charge			+0.86902		
O shell charge			−2.86902		
Three-body potential for O-Si-O and O-Al-O (k_b)			2.09724 eV rad^{-2}		

Note: The methods of derivation are empirical (EMP), modified electron gas (MEG), and Hartree-Fock (HF). References: a = Post and Burnham (1986); b = Sanders et al. (1984); c = James (1979); d = Catlow (1977); e = Walker (personal communication); f = Parker (1983); and g = Lewis and Catlow (1985).

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Table 2. Calculated bond lengths and bond angles of low albite compared with the observed results of Harlow and Brown (1980)

	Obs		2BRI		3BSM1		3BSM2	
a	8.142		8.375		8.461		8.146	
b	12.785		12.978		12.889		12.748	
c	7.159		7.220		7.142		7.070	
α	94.19		95.38		91.10		93.68	
β	116.61		116.57		116.12		116.66	
γ	87.68		87.34		87.86		88.02	
Lattice energy/eV			−2044.81		−1926.86		−1929.87	
T1o-Oa1	1.747		1.721		1.739		1.742	
T1o-Obo	1.745		1.719		1.723		1.731	
T1o-Oco	1.735		1.721		1.740		1.735	
T1o-Odo	1.745		1.740		1.731		1.739	
Oa-Ob	2.713	100.75	2.811	109.56	2.714	103.26	2.684	101.21
Oa-Oc	3.042	120.03	2.802	108.97	2.957	116.43	2.994	118.90
Oa-Od	2.735	101.88	2.877	112.44	2.721	103.25	2.698	101.63
Ob-Oc	2.888	112.21	2.930	116.79	2.881	112.58	2.867	111.61
Ob-Od	2.878	111.16	2.809	108.57	2.864	112.03	2.883	112.41
Oc-Od	2.852	110.08	2.657	100.31	2.824	108.91	2.859	110.50
T1m-Oa1	1.596		1.558		1.582		1.590	
T1m-Obm	1.600		1.577		1.600		1.591	
T1m-Ocm	1.621		1.600		1.629		1.630	
T1m-Odm	1.618		1.597		1.626		1.614	
Oa-Ob	2.608	107.82	2.632	112.62	2.561	107.21	2.584	108.66
Oa-Oc	2.587	116.43	2.787	110.01	2.706	114.85	2.682	112.77
Oa-Od	2.624	105.04	2.599	112.53	2.557	105.68	2.555	105.79
Ob-Oc	2.664	108.23	2.610	113.96	2.629	108.99	2.604	107.92
Ob-Od	2.525	111.31	2.657	105.43	2.683	112.56	2.683	113.70
Oc-Od	2.480	108.03	2.621	101.75	2.628	107.64	2.626	108.11
T2o-Oa2	1.632		1.591		1.629		1.641	
T2o-Obo	1.592		1.565		1.572		1.580	
T2o-Ocm	1.617		1.580		1.629		1.620	
T2o-Odm	1.619		1.597		1.626		1.617	
Oa-Ob	2.660	111.15	2.617	112.07	2.659	112.34	2.663	111.54
Oa-Oc	2.565	104.28	2.701	116.85	2.540	102.41	2.553	103.08
Oa-Od	2.611	107.06	2.542	105.76	2.604	106.31	2.593	105.52
Ob-Oc	2.661	112.06	2.558	108.88	2.650	111.73	2.657	112.24
Ob-Od	2.652	111.60	2.508	104.96	2.674	113.37	2.655	112.31
Oc-Od	2.653	110.34	2.562	107.49	2.666	110.01	2.677	111.58
T2m-Oa2	1.645		1.608		1.655		1.660	
T2m-Obm	1.621		1.607		1.632		1.625	
T2m-Oco	1.596		1.544		1.587		1.583	
T2m-Odo	1.602		1.572		1.583		1.592	
Oa-Ob	2.628	107.21	2.563	105.72	2.630	106.30	2.644	107.24
Oa-Oc	2.588	105.97	2.677	116.24	2.547	103.52	2.576	105.17
Oa-Od	2.635	108.51	2.567	107.67	2.646	109.58	2.654	109.37
Ob-Oc	2.637	110.14	2.548	107.93	2.622	109.07	2.612	109.04
Ob-Od	2.643	110.22	2.527	105.30	2.668	112.11	2.642	110.44
Oc-Od	2.688	114.45	2.601	113.18	2.682	115.53	2.681	115.19
T1o-Oa1-T1m	141.45		148.69		140.45		137.15	
T2m-Oa2-T2o	130.08		143.49		134.49		129.10	
T1o-Obo-T2o	139.66		147.57		146.87		139.58	
T1m-Obm-T2m	161.20		165.79		153.41		158.77	
T1o-Oco-T2m	129.88		142.12		130.52		130.46	
T1m-Ocm-T2o	135.85		149.97		143.70		134.69	
T1o-Odo-T2m	133.95		141.90		139.39		134.36	
T1m-Odm-T2o	151.84		160.44		153.41		150.01	

Note: For each tetrahedron the O-O bond lengths are followed by the O-T-O bond angles (lengths in Å; angles in degrees). Lattice energy is for the unit cell.

tance. The method for calculating the Coulombic interaction of the ions uses the Ewald transformation to allow rapid convergence. Details of the implementation of the method in our lattice energy codes are given by Catlow and Norgett (1976).

It is, of course, necessary to include short-range interactions that are described by effective potentials. Buckingham potentials have been used exclusively within this study to model the central force component of these interactions. The form of this potential is given by

$$U_R = \frac{1}{2} \sum_{i}^{\text{one cell}} \sum_{j \neq i}^{\text{all cells}} A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij} r^{-6}. \qquad (2)$$

The exponential term arises from repulsive interaction of the electron clouds as the atoms approach. The r^{-6} term accounts for short-range dispersive attractions. It is common practice to use a cutoff value beyond which the short-range forces are assumed to be negligible. The value used throughout this paper is 10.0 Å.

Interatomic potentials can be obtained either by fitting

TABLE 3. Calculated bond lengths and bond angles of microcline compared with the observed results of Brown and Bailey (1964)

	Obs	2BRI	3BSM1	3BSM2
a	8.560	8.657	9.162	8.580
b	12.964	13.062	12.829	12.897
c	7.215	7.305	7.263	7.139
α	90.39	92.83	90.40	90.36
β	115.50	115.59	115.37	116.04
γ	87.42	87.24	88.27	87.85
lattice energy/eV		−2042.95	−1921.61	−1927.52
T1o-Oa1	1.738	1.722	1.741	1.736
T1o-Obo	1.739	1.718	1.727	1.721
T1o-Oco	1.745	1.738	1.748	1.742
T1o-Odo	1.741	1.736	1.737	1.730
O-T1-O	109.43	109.42(4.4–9.2)	109.44(0.1–1.3)	109.42(0.1–2.3)
O-O	2.841	2.817(2.0–6.9)	2.837(0.1–1.3)	2.825(0.0–1.5)
T1m-Oa1	1.592	1.551	1.578	1.579
T1m-Obm	1.608	1.578	1.610	1.603
T1m-Ocm	1.629	1.599	1.644	1.631
T1m-Odm	1.627	1.606	1.636	1.629
O-T1m-O	109.48	109.38(3.9–6.9)	109.46(0.0–1.5)	109.49(0.5–1.7)
O-O	2.636	2.582(0.3–6.5)	2.640(0.1–0.5)	2.629(0.2–1.5)
T2o-Oa2	1.614	1.586	1.622	1.623
T2o-Obo	1.574	1.559	1.571	1.571
T2o-Ocm	1.633	1.583	1.646	1.632
T2o-Odm	1.621	1.601	1.628	1.628
O-T2o-O	109.42	109.39(0.4–10.7)	109.36(0.0–2.7)	109.37(0.2–1.5)
O-O	2.636	2.582(1.0–4.9)	2.640(0.2–1.9)	2.629(0.0–1.1)
T2m-Oa2	1.644	1.609	1.650	1.651
T2m-Obm	1.617	1.607	1.639	1.635
T2m-Oco	1.593	1.547	1.594	1.588
T2m-Odo	1.592	1.563	1.583	1.581
O-T2m-O	109.38	109.38(0.2–9.1)	109.39(0.2–2.8)	109.34(0.4–1.3)
O-O	2.628	2.580(1.2–4.4)	2.637(0.2–1.8)	2.631(0.1–1.0)
T1o-Oa1-T1m	144.69	151.31	143.20	141.00
T2o-Oa2-T2m	138.47	149.62	145.30	136.58
T1o-Obo-T2o	151.16	155.28	147.33	147.78
T1m-Obm-T2m	155.95	164.37	149.89	151.64
T1o-Oco-T2m	130.71	138.32	129.97	130.20
T2o-Ocm-T1m	130.68	148.77	130.43	131.78
T1o-Odo-T2m	139.99	146.48	138.23	140.59
T2o-Odm-T1m	143.19	154.79	139.73	141.97

Note: The O-O distances and O-T-O bond angles are given as an average for each TO_4 tetrahedron with the minimum and maximum percentage differences in brackets (lengths in Å; angles in degrees). Lattice energy is for the unit cell.

the observed crystal properties or from theoretical methods. Among the latter, electron gas (EG) and modified electron gas (MEG) methods have enjoyed considerable success. The MEG potentials of Post and Burnham (1986) are employed in the present study. Indeed in the two-body rigid-ion calculations (2BRI), all parameters were based on Post and Burnham's study, whereas in the three-body shell model calculations, discussed below, both empirical and MEG potentials were used. All potential parameters employed in this study are reported in Table 1. Note that in modeling interactions between the framework species and the extra-framework cations, short-range terms are included only for cation-O interactions; interactions between tetrahedral atoms and extra-framework species are assumed to be purely Coulombic.

The second model (3BSM) is similar to the first but includes three-body and polarization terms. The latter are described using the shell model of Dick and Overhauser (1958). Sanders et al. (1984) demonstrated the inadequacy of two-body models when applied to α-SiO_2 and showed that it is necessary to include a bond-bending term to account for covalent forces acting within the crystal. The bond-bending term (which is coupled to the shell) has the form

$$U_B = \frac{1}{2} \sum_{i,j,k} k_{b,ijk} (\theta_{ijk} - \theta_o)^2 \tag{3}$$

where $(\theta_{ijk} - \theta_o)$ is the deviation of the bond angle from an ideal bond angle and k_b is a harmonic force constant. In the work of Sanders et al. (1984) the three-body terms were applied around the O-Si-O bond angles in α-quartz. These authors suggested that this term describes "the rigidity that is conferred upon the SiO_4 tetrahedra by the component of sp^3 hybridized, covalent bonding around the Si atom." It is assumed that the electronic environment of the Si and O atoms in feldspars is not significantly different from that in quartz and that the potentials derived by Sanders et al. (1984) can be used without modification in this study. Jackson and Catlow in their study of zeolites (1988) demonstrated that this three-body force constant can also be used for O-Al-O bond angles in aluminosilicates.

The potentials between framework O atoms and extra-

TABLE 4. Observed and calculated bond lengths for anorthite

	Obs	Calc		Obs	Calc
T1(0000)-Oa(1000)	1.645	1.650	T1(0z00)-Oa(1z00)	1.760	1.753
-Ob(0000)	1.619	1.632	-Ob(0z00)	1.743	1.734
-Oc(0000)	1.582	1.579	-Oc(0z00)	1.709	1.710
-Od(0000)	1.616	1.627	-Od(0z00)	1.776	1.773
T1(00i0)-Oa(10i0)	1.632	1.630	T1(0zi0)-Oa(1zi0)	1.772	1.765
-Ob(00i0)	1.606	1.617	-Ob(0zi0)	1.755	1.772
-Oc(00i0)	1.588	1.587	-Oc(0zi0)	1.727	1.725
-Od(00i0)	1.626	1.640	-Od(0zi0)	1.767	1.759
T1(mz00)-Oa(1z00)	1.647	1.657	T1(m000)-Oa(1000)	1.777	1.761
-Ob(mz00)	1.617	1.620	-Ob(m000)	1.705	1.677
-Oc(mz00)	1.617	1.633	-Oc(m000)	1.738	1.732
-Od(mz00)	1.571	1.567	-Od(m000)	1.779	1.764
T1(mzi0)-Oa(1xi0)	1.644	1.657	T1(m0i0)-Oa(10i0)	1.777	1.761
-Ob(mzi0)	1.583	1.567	-Ob(m0i0)	1.747	1.747
-Oc(mzi0)	1.599	1.605	-Oc(m0i0)	1.752	1.749
-Od(mzi0)	1.626	1.630	-Od(m0i0)	1.702	1.676
T2(0z00)-Oa(2z00)	1.635	1.647	T2(0000)-Oa(2000)	1.760	1.780
-Ob(0z00)	1.620	1.624	-Ob(0000)	1.769	1.762
-Oc(m0i0)	1.606	1.607	-Oc(mzi0)	1.740	1.733
-Od(m000)	1.605	1.610	-Od(mz00)	1.698	1.685
T2(0zi0)-Oa(2zi0)	1.617	1.647	T2(00i0)-Oa(20i0)	1.769	1.777
-Ob(0zi0)	1.628	1.640	-Ob(00i0)	1.751	1.745
-Oc(m000)	1.614	1.603	-Oc(mz00)	1.754	1.754
-Od(m0i0)	1.574	1.577	-Od(mzi0)	1.727	1.723
T2(m000)-Oa(2000)	1.644	1.649	T2(mz00)-Oa(2000)	1.755	1.758
-Ob(m000)	1.581	1.577	-Ob(mz00)	1.748	1.736
-Oc(0zi0)	1.607	1.602	-Oc(00i0)	1.716	1.719
-Od(0z00)	1.629	1.645	-Od(0000)	1.757	1.751
T2(m0i0)-Oa(20i0)	1.641	1.648	T2(mzi0)-Oa(2zi0)	1.759	1.759
-Ob(m0i0)	1.618	1.622	-Ob(mzi0)	1.711	1.682
-Oc(0z00)	1.586	1.589	-Oc(0000)	1.733	1.724
-Od(0zi0)	1.616	1.629	-Od(00i0)	1.775	1.771
Ca(000)-Oa(1000)	2.608	2.479	Ca(z00)-Oa(1z00)	2.496	2.442
-Oa(1000)	2.515	2.436	-Oa(1z00)	2.733	2.578
-Oa(2000)	2.292	2.209	-Oa(2z00)	2.333	2.231
-Ob(0000)	2.378	2.285	-Ob(0z00)	2.443	2.324
-Od(mz00)	2.390	2.290	-Ob(mz00)	2.494	2.423
-Od(m000)	2.538	2.409	-Oc(m0i0)	2.559	2.532
			-Od(0z00)	2.372	2.363
Ca(0i0)-Oa(10i0)	2.448	2.392	Ca(zi0)-Oa(1zi0)	2.454	2.481
-Oa(10i0)	2.817	2.823	-Oa(1zi0)	2.616	2.353
-Oa(20i0)	2.336	2.213	-Oa(2zi0)	2.300	2.213
-Ob(00i0)	2.426	2.304	-Ob(0zi0)	2.405	2.253
-Ob(m0i0)	2.494	2.368	-Oc(m000)	2.833	2.309
-Oc(mz00)	2.563	2.445	-Od(0zi0)	2.440	2.501
-Od(00i0)	2.434	2.305	-Od(mzi0)	2.717	2.928

Note: The experimental data are from Wainwright and Starkey (1971); calculations employed the three-body shell model and the Ca-O potential of Post and Burnham (1986); lengths in Å.

framework cations were of two types: first, empirical potentials were used from a variety of sources (Model 3BSM1); second, the Post and Burnham cation-O parameters were used (Model 3BSM2).

As noted, ionic polarization of the O atom can be simulated by the use of a shell model, in which a massless shell is connected by a harmonic spring to the core, in which the atomic mass is concentrated, thus:

$$U_s = k_s r^2 \tag{4}$$

where U_s is the core-shell interaction energy, k_s is the spring constant, and r is the core-shell separation. The free-ion polarizability (α) is given by

$$\alpha = Y^2/k_s \tag{5}$$

where Y is the shell charge.

RESULTS

Two-body models

Lattice-energy minimization calculations using the 2BRI model employed the potentials of Post and Burnham (1986, 1987). Detailed results for albite and microcline are presented in Tables 2 and 3, which give calculated and experimental bond lengths and bond angles for framework species. Detailed results are not reported for anorthite using the 2BRI model, but the level of agreement is very similar to that obtained with the other two structures.

For low albite the energy minimization produced bond lengths very similar to those given by Post and Burnham (1987). As those authors pointed out, the Al-O, Si-O, and O-O bond lengths are a little too short, as is clear from the results presented in Tables 2 and 3. The unit-cell

TABLE 5. Cation-oxygen bond lengths for albite and microcline for the two three-body shell model calculations (3BSM1 and 3BSM2)

	Obs	3BSM1	3BSM2
Na-Oa1(0000)	2.671	2.708	2.565
Na-Oa1(000c)	2.537	2.773	2.521
Na-Oa2(0000)	2.372	2.626	2.363
Na-Oa2(000c)	3.724	3.503	3.649
Na-Oa2(000c)	3.725	3.792	3.726
Na-Ob(000c)	2.461	2.482	2.456
Na-Ob(m00c)	3.465	3.158	3.317
Na-Oc(0zi0)	2.996	2.904	3.004
Na-Oc(mzi0)	3.266	3.315	3.215
Na-Od(0000)	2.437	2.755	2.415
Na-Od(m000)	2.996	2.919	2.993
K-Oa1	2.877	3.192	2.833
K-Oa1	2.881	3.295	2.850
K-Oa2	2.750	3.334	2.744
K-Oa2	3.402	3.187	3.386
K-Obo	2.961	3.378	2.930
K-Obm	3.136	3.511	3.083
K-Oco	2.907	3.007	2.892
K-Ocm	3.335	3.253	3.340
K-Odo	2.892	2.994	2.865
K-Odm	2.993	3.167	2.941

Note: Bond lengths in Å.

parameters are, however, in reasonably good agreement with the observed values. However, the 2BRI model is not able to reproduce accurately the O-T-O and T-O-T bond angles. The distortions within the tetrahedra are not correctly reproduced, whereas the T-O-T angles are consistently too large. The calculations for microcline (Table 3) and anorthite exhibit similar characteristics. The maximum percentage differences between calculated and observed values for the O-T-O and T-O-T bond angles are 10.7% and 13.8%, respectively, for microcline. The poor reproduction of T-O-T angles in α-quartz (which are also too large, giving a structure similar to that of β-quartz) has been noted by numerous authors and has been attributed to the omission of angle-dependent forces within the simulation, as discussed by Sanders et al. (1984).

TABLE 6. Calculated and observed O-T-O and T-O-T bond angles (within fourfold rings) in anorthite

		Oa-Ob	Oa-Oc	Oa-Od	Ob-Oc	Ob-Od	Oc-Od
T1(0000)	obs	100.90	118.07	101.40	111.73	113.80	110.44
T1(0000)	calc	97.80	122.50	98.42	111.41	115.24	110.79
T1(00i0)	obs	103.09	116.38	102.05	110.92	113.56	110.51
T1(00i0)	calc	102.52	119.53	99.63	110.18	115.33	109.50
T1(mz00)	obs	100.78	113.70	108.85	111.38	113.45	108.61
T1(mz00)	calc	98.42	115.19	107.58	111.67	116.90	107.15
T1(mzi0)	obs	106.15	112.27	102.08	113.14	112.06	110.54
T1(mzi0)	calc	106.74	112.67	99.49	114.00	112.47	110.53
T2(0z00)	obs	105.34	101.24	110.17	112.51	111.79	114.83
T2(0z00)	calc	103.90	98.89	109.73	112.89	112.22	117.41
T2(0zi0)	obs	109.19	102.50	110.99	112.86	107.14	114.10
T2(0zi0)	calc	110.75	101.35	111.53	114.52	102.77	116.21
T2(m000)	obs	111.89	104.43	108.95	112.98	107.26	111.33
T2(m000)	calc	113.73	104.60	109.32	113.46	104.40	111.44
T2(m0i0)	obs	108.79	106.37	107.89	112.60	108.75	112.27
T2(m0i0)	calc	107.75	107.97	106.75	111.80	109.73	112.59
T1(0z00)	obs	99.75	117.51	98.98	112.77	115.60	111.25
T1(0z00)	calc	97.34	120.44	95.71	111.81	122.73	112.52
T1(0zi0)	obs	97.25	121.03	97.16	113.20	116.44	110.66
T1(0zi0)	calc	94.06	122.85	93.23	112.68	119.44	112.70
T1(m000)	obs	107.57	112.19	99.12	114.34	111.15	111.40
T1(m000)	calc	109.57	112.03	96.32	114.15	111.84	111.58
T1(m0i0)	obs	99.28	113.08	108.52	113.59	113.26	108.83
T1(m0i0)	calc	96.62	113.29	109.83	112.82	113.93	109.82
T2(0000)	obs	108.87	104.12	107.84	112.63	108.08	115.02
T2(0000)	calc	109.17	102.61	107.97	113.33	108.55	114.85
T2(00i0)	obs	100.96	99.94	107.64	112.74	115.95	116.74
T2(00i0)	calc	99.11	95.71	107.17	112.31	118.81	119.14
T2(mz00)	obs	108.59	105.69	103.15	110.45	111.95	116.30
T2(mz00)	calc	108.56	105.56	102.11	112.51	112.50	115.01
T2(mzi0)	obs	110.32	105.24	107.35	111.99	108.71	113.09
T2(mzi0)	calc	111.68	105.27	107.69	111.69	109.31	111.10

Atom	Obs angle	Calc angle	Atom	Obs angle	Calc angle
Ob(0000)	129.41	126.37	Ob(0z00)	138.79	136.07
Od(0000)	136.45	133.33	Od(0z00)	123.67	120.39
Ob(mz0c)	144.07	141.45	Ob(m00c)	169.93	174.66
Od(mz0c)	165.21	165.57	Od(m00c)	139.70	136.16
Ob(m0i0)	145.76	140.67	Ob(mzi0)	165.67	168.18
Od(m0i0)	165.08	174.02	Od(mzi0)	136.14	132.87
Ob(0zic)	126.88	120.40	Ob(00ic)	137.61	133.46
Od(0zic)	135.01	133.24	Od(00ic)	127.15	124.60

Note: Potential model as in Table 5; angles in degrees.

Three-body models

Lattice-energy minimization of the albite, microcline, and anorthite structures using the 3BSM model gives bond lengths similar to the observed results (Tables 2, 3, and 4). Improved Si-O and Al-O bond lengths are obtained, as the empirical potentials give a better description of the short-range interactions. However, the Si-O bond length within a Si-O-Al unit is slightly but consistently short, indicating that the Si-O-Al interaction is not perfectly modeled. More important, however, is the finding that by including the three-body potential, the O-O bond lengths and the O-T-O and T-O-T bond angles are greatly improved. Calculations for all three minerals were carried out using the purely empirical potentials (3BSM1) and the potentials in which MEG parameters were used for the extra-framework cation-O interaction (3BSM2). Si-O and Al-O bond lengths within the 3BSM2 model tend to be slightly more accurate, especially for albite. For albite and microcline, the error for O-T-O bond angles and O-O bond lengths using 3BSM2 increases for the T1o tetrahedron and decreases for the T2o and T2m tetrahedra in both minerals.

The cation-O bond lengths for albite and microcline are given in Table 5. The potentials from the MEG calculations are less repulsive, giving rise to shorter cation-O bond lengths. In general, they give more satisfactory results than the empirical models. Thus in albite the less repulsive cation-O potential causes a marked improvement in the T-O-T bond angles, although in microcline only a slight improvement is observed, possibly because the smaller Na^+ ion requires the framework to relax inward around it. Similarly, in anorthite the empirical models raise the symmetry to monoclinic. In contrast, the less repulsive MEG cation potential is able to distort the framework to its correct lower symmetry structure, as shown by the calculated bond angles for anorthite given in Table 6. Indeed the model can reproduce the strong distortions within the tetrahedra of anorthite, as shown by the calculated bond angles given in Table 6.

DISCUSSION AND CONCLUSIONS

The ability to reproduce the Al-O and Si-O bond lengths by lattice-energy minimization is largely controlled by the accuracy of the Buckingham potential describing the two-body component of the short-range repulsive forces. The accurate modeling of bond angles and of the O-O bond length requires that angle-dependent terms and polarization be included in the potential. Thus, the 2BRI model is unsuccessful in producing accurate results. The inclusion of polarization effects and three-body terms for the O-T-O angle effects a considerable improvement. The 3BSM model is capable of simulating the large range of T-O-T and O-T-O bond angles observed in the feldspar minerals. We found that the T-O-T bond angle is very sensitive to the influence of the cation-O short-range potential, whereas the O-T-O bond angle is fairly insensitive.

The MEG potentials for cation-O interactions developed by Post and Burnham perform significantly better in this respect than do the various empirical cation-O potentials, and their use should be encouraged in future studies of feldspars.

Overall, the simulations reported in this paper show that feldspar structures can be accurately modeled by available three-body shell model potentials for framework interactions and MEG potentials for interactions between extra-framework cations and O atoms. More subtle problems relating to defects and to the energetics of various Si-Al distributions are now amenable to study.

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