Mechanisms and geochemical significance of Si–Al substitution in zeolite solid solutions

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Abstract

Rock-forming zeolites often exhibit complex solid solutions reflecting isomorphous substitutions between Si and Al in tetrahedral framework sites, between charge-balancing extraframework cations, and between water molecules and vacancies. Although the number of moles of charge on extraframework cations in a zeolite must equal the moles of Al in order to maintain charge balance, the relationships between Si–Al and extraframework substitutions vary considerably across this mineral group. Review of available compositional data suggests that there are three main modes of Si–Al substitution in zeolites: 1) coupled CaAl–NaSi substitution; 2) coupled substitution of a single extraframework cation plus Al for Si; and 3) completely uncoupled substitution among extraframework cations and Si and Al on tetrahedral sites. Among zeolites that exhibit the latter two modes of solid solution, Si–Al substitution can be described by an SiO_2 ($\pm H_2O$) compositional exchange vector from a hypothetical, pure-silica endmember composition. Recent calorimetric, structural, and theoretical investigations suggest that Si–Al substitution follows a non-ideal, athermal solution model characterized by no excess enthalpies of mixing and negative excess entropies of mixing. Because Si–Al exchange in these minerals can be explicitly or implicitly described by exchange of an SiO_2 component, the Si/Al ratio in their framework can be predicted solely as a function of temperature, pressure, and the chemical potential of SiO_2. Application of this model leads to calculated Si/Al ratios in stilbite (coexisting with albite), analcime, and chabazite consistent with observed mineral compositions and parageneses in very low-grade metamorphic environments. Coexistence of silica polymorphs with zeolites containing $SiO_2 \cdot nH_2O$ exchange vectors potentially provides a means of performing thermobarometric calculations in very low-grade metamorphic and diagenetic environments.
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1. Introduction

Zeolites are important rock-forming minerals in a wide range of geologic environments, including soils, lacustrine sediments, sedimentary basins, low-grade metavolcanic rocks, alkaline intrusions, and silica-deficient lavas (e.g., Gottardi and Galli, 1985; reviews in Bish and Ming, 2001). Their widespread occurrence is largely a consequence of their mineralogical diversity (Coombs et al., 1997; Armbruster and Gunter, 2001) and extensive solid solutions (Passaglia and Sheppard, 2001). It is now widely recognized that the distribution of individual zeolite minerals within a given geologic setting can provide a sensitive record of temperature, pressure, or chemical conditions during formation (e.g., Iijima, 1988; Kristmannsdóttir and Tómasson, 1978; Hay, 1966; Noh and Boles, 1993; Donahoe et al., 1984; Bowers and Burns, 1990; Abercrombie et al.,

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1994; Neuhoff et al., 2000; Chipera and Apps, 2001). In addition, a few studies point to systematic variations in the composition of individual zeolites as a function of temperature and/or pressure (e.g., Fridriksson et al., 2001; Ogihara, 1996; Iijima, 1988). Zeolites thus have the potential to provide a wealth of information about in situ conditions under which rock-forming processes occur.

Quantitative prediction of the stability and composition of zeolites as a function of temperature, pressure, and system composition in natural systems is hampered in large part by incomplete knowledge of substitution mechanisms and thermodynamic properties in zeolite solid solutions. The most thoroughly investigated solid solutions in zeolites involve a) substitution between water molecules and vacancies within zeolite channels (e.g., van Reeuwijk, 1974; Bish and Carey, 2001) and b) substitution of ions on extraframework sites, which is readily achieved through ion exchange (e.g., review in Pabalan and Bertetti, 2001). In the case of the latter solid solutions, relatively few studies have investigated the behavior of these solutions as a function of temperature and pressure, and rarely have the results been used to interpret natural mineral parageneses (although see Fridriksson et al., 2004). Considerably less is known about Si–Al substitution in zeolites, although recent calorimetric, compositional, and spectroscopic studies have begun to address the mechanisms and energetics of this type of solutions (e.g., Petrovic and Navrotsky, 1997; Shim et al., 1999; Neuhoff et al., 2003, 2004). In cases where substitution mechanisms are understood and the thermodynamic properties have been determined, quantitative models of the stability of zeolite solid solutions as a function of temperature, pressure and chemical potential have provided a valuable tool for interpreting geochemical systems (e.g., Fridriksson et al., 2001; Neuhoff and Bird, 2001; Neuhoff et al., 2004).

In the present communication, we review the current state of knowledge about the compositions and substitution mechanisms in rock-forming zeolites. We propose four rules governing the potential coupling of Si–Al and extraframework solutions in zeolites and discuss the current state of understanding concerning the energetics of these types of solid solutions. This information is then used to develop conceptual and quantitative models of the controls on zeolite composition in natural systems, with specific reference to the potential to use zeolite compositions as indicators of thermobarometric conditions and silica activity.

2. Crystal chemical constraints on zeolite solid solutions

Zeolites are tectosilicates characterized by open frameworks consisting of SiO_4 and AlO_4 tetrahedra connected to form three-dimensional networks surrounding cages and channels within the crystal structure (Coombs et al., 1997). The negative framework charge caused by the presence of Al in tetrahedral sites requires charge-compensation by extraframework cations within the cages and channels, typically of alkali metal and alkaline earth elements (e.g., Na^+, K^+, Ca^{2+}, Ba^{2+}, Sr^{2+}, Cs^+, and Mg^{2+}). Additionally, water molecules are present in extraframework positions as well. The general formula of zeolites can thus be written as $(A^{+z})_{y/z}(Al^{3+})_y(Si)_x O_{2(x+y)} \cdot nH_2O$ where A represents extraframework cations, z is the charge on the extraframework cations, n is the number of moles of molecular water, and x and y are the stoichiometric coefficients for Al^{3+} and Si^{4+} in tetrahedral sites, respectively. In some zeolites, substitution of Fe^{3+} or Be^{3+} occurs in the tetrahedral sites but is ignored here as the extent of these substitutions tends to be limited.

The extent of framework and extraframework solid solution in zeolites, though often extensive, is limited by volumetric, site connectivity, and charge balance constraints within their structures. Framework Si/Al ratios in natural zeolites range from 1 to ~5 (Passaglia and Sheppard, 2001), with compositions of synthetic zeolites extending all the way to pure SiO_2 forms (e.g., Woodcock et al., 1999). The lower limit on Si/Al ratio is a consequence of the tendency for Al avoidance (i.e., avoidance of Al–O–Al linkages within the structure; Loewenstein, 1954) that can only be achieved at compositions with at least as much Si as Al. In some structures, the three-dimensional connectivity of the tetrahedra and Si–Al ordering between sites may further restrict the range of observed Si/Al ratio (Neuhoff and Stebbins, 2001; Neuhoff et al., 2003). The amount of charge present on the extraframework sites is fixed by charge balance requirements to be equal to the amount of Al in the framework. The availability of space within the extraframework channels and cages in the structure further limits the size of extraframework cations that can be accommodated on individual sites within the structure and the total number of extraframework species (i.e., cations and water molecules).

While charge balance and structural constraints limit the range of substitutions observed in zeolites there exists some controversy as to whether substitutions between framework and extraframework sites follow discrete substitutional rules as observed in other frame-

work silicates (for instance, the coupled CaAl–NaSi substitution observed in plagioclase feldspars). Recent reviews of zeolite composition have stressed the lack of coupling between Si–Al and extraframework substitutions because of the ease of modification of extraframework cation contents by ion exchange (e.g., Mumpton, 1978; Passaglia and Sheppard, 2001). Often, however, there is insufficient data at present to fully assess the extent of substitutions observed in many zeolites. As more compositional data become available, it is apparent that zeolite exhibit several distinct behaviors with respect to the degree of Si–Al substitution and how charge balance is maintained through changing extraframework cation occupancy as Si/Al varies. Based on published interpretations of zeolite crystal chemistry and our own analyses of published mineral compositions, we propose that rock-forming zeolites exhibit

four distinct modes of Si–Al substitution that are detailed below. Table 1 lists the compositions of the rock-forming zeolites discussed below, arranged in terms of their Si–Al substitution mode.

2.1. Mode I: zeolites exhibiting limited Si–Al substitution

Several important rock-forming zeolite species exhibit virtually no variation in Si/Al ratio or in the their extraframework cation contents. Examples of this behavior include laumontite ($CaAl_2Si_4O_{12} \cdot nH_2O$), long-range Si–Al ordered wairakite ($CaAl_2Si_4O_{12} \cdot nH_2O$), bikitaite ($LiAlSi_2O_6 \cdot nH_2O$), yugawaralite ($CaAl_2Si_6 O_{16} \cdot nH_2O$), and the Si–Al ordered NAT topology zeolites (natrolite, mesolite, and scolecite; $Na_2Al_2Si_3O_{10} \cdot n H_2O$, $Na_{0.667}Ca_{0.667}Al_2Si_3O_{10} \cdot nH_2O$, and $CaAl_2Si_3$

Table 1
Proposed Si–Al substitution mode and compositional ranges (Passaglia and Sheppard, 2001 unless otherwise noted) for zeolites discussed in text

Mode I

Mineral	Composition
Laumontite	$CaAl_2Si_4O_{12} \cdot nH_2O$
Wairakite	$CaAl_2Si_4O_{12} \cdot nH_2O$
Bikitaite	$LiAlSi_2O_{12} \cdot nH_2O$
Yugawaralite	$CaAl_2Si_6O_{16} \cdot nH_2O$
Natrolite	$Na_2Al_2Si_3O_{10} \cdot nH_2O$
Mesolite	$Na_{0.667}Ca_{0.667}Al_2Si_3O_{10} \cdot nH_2O$
Scolecite	$CaAl_2Si_3O_{10} \cdot nH_2O$

Mode II

Mineral	CaAl-rich endmember	NaSi-rich endmember	References[a]
Thomsonite	$Ca_2NaAl_5Si_5O_{20} \cdot 6H_2O$	$Ca_{1.5}Na_{1.5}Al_{4.5}Si_{5.5}O_{20} \cdot 5H_2O$	R92, F65
Phillipsite	$K_2Ca_2Al_6Si_{10}O_{32} \cdot nH_2O$	$K_2Na_2Al_4Si_{12}O_{32} \cdot nH_2O$	GG72
Gonnardite	$CaNa_3Al_5Si_5O_{20} \cdot nH_2O$	$Na_4Al_4Si_6O_{20} \cdot nH_2O$	R92[b]

Mode III

Mineral	NaAl-rich endmember	Si-rich endmember	References[a]
Stilbite–stellerite	$CaNa_{0.5}Al_{2.5}Si_{6.5}O_{18} \cdot 8H_2O$	$CaAl_2Si_7O_{18} \cdot 7H_2O$	F01, P78
Low analcime	$Na_{1.05}Al_{1.05}Si_{1.95}O_6 \cdot 0.975H_2O$	$Na_{0.75}Al_{0.75}Si_{2.25}O_6 \cdot 1.125H_2O$	N04

Mode IV

Mineral	Si/Al ratio	Extraframework cations
Chabazite	1.4–4.3	Na, Ca, K
High analcime–pollucite	1.4–3.0	Na, Cs, K, Rb, Ca
Mordenite	4.0–6.1	Na, Ca, K
Heulandite–clinoptilolite	2.7–5.7	Na, Ca, K, Sr, Ba
Gonnardite	1.1–2.3	Na, Ca, K
Offretite	2.2–2.6	K, Na, Ca, Mg
Erionite	2.3–3.4	K, Na, Ca, Mg
Phillipsite	1.3–3.3	K, Na, Ca

[a] Key to references: F01 (Fridriksson et al., 2001), F65 (Foster, 1965), GG72 (Galli and Ghittoni, 1972), N04 (Neuhoff et al., 2004), P78 (Passaglia et al., 1978), R92 (Ross et al., 1992).
[b] Represents the "tetranatrolite" series defined by Ross et al. (1992).

$O_{10} \cdot nH_2O$, respectively). The common feature of all of the zeolites exhibiting Mode I behavior is that they exhibit large degrees of Si–Al order among crystallographically and energetically distinct tetrahedral sites (e.g., Armbruster and Gunter, 2001; Alberti, 1991). The extent of Si–Al substitution is limited by the multiplicity of sites in the structure, and local charge balance and volumetric constraints lead to preferential occupancy of the extraframework cation sites by one type of cation. It should be noted that gonnardite, which shares the NAT framework topology with natrolite, mesolite, and scolecite but is Si–Al disordered, exhibits much greater compositional variation, with Si/ Al ratios ranging from 1 to ~1.5 and Na/(Na+Ca) ranging from 0.65 to 1 (Artioli and Galli, 1999) and is discussed below.

2.2. Mode II: zeolites with coupled CaAl–NaSi substitutions such as those observed in plagioclase feldspars

A common mode of charge-balancing accompanying Si–Al substitution in tectosilicates is coupled substitution of $(Ca^{2+}+Al^{3+})$ for $(Na^{+}+Si^{4+})$ as observed in plagioclase feldspars where a discrete sold solution exists between anorthite $(CaAl_2Si_2O_8)$ and albite $(NaAlSi_3O_8)$. The clearest example of this behavior among zeolites is thomsonite, which comprises a series between the compositions $Ca_2NaAl_5Si_5O_{20} \cdot nH_2O$ and $Ca_{1.5}Na_{1.5}Al_{4.5}Si_{5.5}O_{20} \cdot nH_2O$ (Fig. 1 and Ross et al., 1992; Foster, 1965). Substitution of Ca for Na in thomsonite occurs on one of the two distinct extraframework cation sites (the other being fully occupied by Ca; Ross et al., 1992).

Ross et al. (1992) have proposed that "tetranatrolite" (a discredited variety of gonnardite) also exhibits CaAl– NaSi substitution between the compositions $Na_4Al_4Si_6O_{20} \cdot nH_2O$ and $CaNa_3Al_5Si_5O_{20} \cdot nH_2O$. This model, and a related series proposed by the same authors for gonnardite that involves coupled $Na_3Si–Ca_2Al$ exchange (a series between $Na_4Al_4Si_6O_{20} \cdot nH_2O$ and $Ca_2NaAl_5Si_5O_{20} \cdot nH_2O$), remains controversial in light of numerous published analyses of gonnardite compositions that do not follow these compositional trends (Artioli and Galli, 1999). Evidence for discrete solid solutions in gonnardite displaying coupled CaAl–NaSi and $Na_3Si–Ca_2Al$ exchange cited by Ross et al. (1992) lies primarily in analyses of samples from two localities, Mont St. Hilaire (Canada) and Magnet Cove (Arkansas, USA) that appear to form a series amongst themselves (Evans et al., 2000). In light of the fact that gonnardite can be cation exchanged (Artioli and Torres-Salvador, 1991), it appears that gonnardite may not
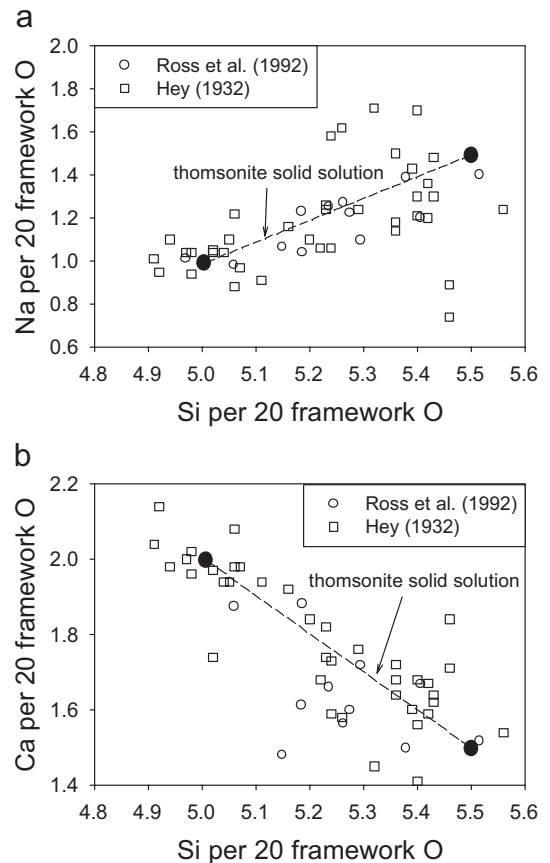

Fig. 1. Compositions of natural thomsonites represented in terms of the number of moles of Na (a) and Ca (b) versus the number of moles of Si on a 20 framework oxygen basis. Open symbols are data from Ross et al. (1992) and Hey (1932) (symbols plotted are analyses selected by Foster, 1965, which exhibit minimal charge imbalance in the reported structure). The large black circles joined by a dashed line represent the proposed endmembers and coupled CaAl–NaSi (Mode II; see text) substitution mechanism, respectively, in thomsonite. Note that the data (particularly those reported and compiled by Hey, 1932) are scattered around the proposed solution, largely representing analytical inaccuracies.

strictly follow Mode II behavior. It may be possible that the compositions of gonnardites in some occurrences are buffered by the presence of other minerals, leading to the trends proposed by Ross et al. (1992), or that a solvus occurs in the system that causes different substitution modes to occur in this mineral. Further systematic study of the chemical composition of gonnardite is clearly needed in order to assess the relationship between framework and extraframework substitutions.

Mode II behavior has also been proposed for phillipsite (Galli and Ghittoni, 1972). In many phillipsite samples, the K content is constant at two atoms per 32 framework oxygens and constitutes roughly 50% of the

extraframework cations (Fig. 2a), and the Ca content is positively correlated with Al (Fig. 2b), leading to a suggested series between $K_2Ca_2Al_6Si_{10}O_{32} \cdot nH_2O$ and $K_2Na_2Al_4Si_{12}O_{32} \cdot nH_2O$ (Galli and Ghittoni, 1972). The limited substitution of Na, and particularly Ca, for K apparent in Fig. 2a is likely a consequence of the large difference in ionic radius between these cations. Review of the data presented by Galli and Ghittoni (1972) indicates that some samples do not conform to this rule as the proportion of K in the extraframework sites deviates significantly from 50% (Fig. 2a). It thus appears that while there is a tendency towards Mode II behavior in phillipsite, this mineral is capable of mode IV behavior discussed below which is consistent with the fact that it is readily ion exchanged
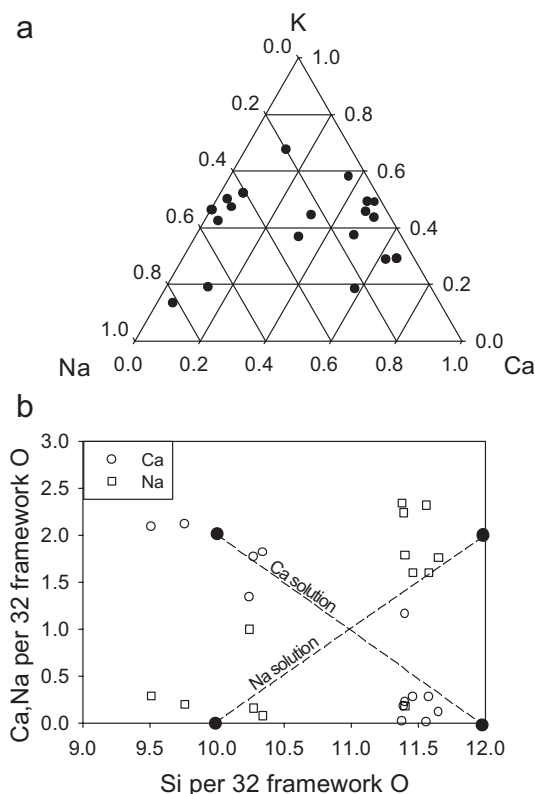

Fig. 2. Compositions of natural phillipsites represented in terms of the relative proportions of Na, Ca, and K in the structure (a) and the number of Na and Ca versus the number of moles of Si on a 32 framework oxygen basis (b). Data in (a) are selected analyses compiled by Galli and Ghittoni (1972) that have charge imbalances less than 0.2 charges per 32 framework oxygens. Data shown by open symbols in (b) are a subset of the analyses shown in (a) for which the proportion of K in the extraframework cation sites is between 0.4 and 0.6, conforming to the proposed Mode II solution model for phillipsite. The large black circles joined by a dashed line represent the proposed endmembers and coupled CaAl–NaSi (Mode II; see text) substitution mechanism, respectively, in phillipsite.

(e.g., Shibue, 1981). Similar compositional ranges are likely present in harmotome, which is isostructural with phillipsite but contains Ba in the K site (Armbruster and Gunter, 2001; Passaglia and Sheppard, 2001). A complete series appears to exist between harmotome and phillipsite defined by K and Ba occupancy on the same site that is accompanied by diminished Ca+Na content in Ba-dominant samples (Passaglia and Sheppard, 2001).

2.3. Mode III: substitution of Al for Si coupled with increased Na occupancy

Increased Al content in zeolites is necessarily accompanied by an increase in extraframework cation occupancy in order to maintain charge balance in the structure. In some zeolites, increased extraframework occupancy is accomplished by substitution of NaAl for Si without appreciable increase in the amount of Ca or other ions. Examples include stilbite–stellerite minerals (forming a series between stellerite, $CaAl_2Si_7O_{18} \cdot nH_2O$ and endmember stilbite, $CaNa_{0.5}Al_{2.5}Si_{6.5}O_{18} \cdot nH_2O$; Fridriksson et al., 2001; Passaglia et al., 1978) and "low" (short-range ordered) analcime (forming a series between $Na_{1.05}Al_{1.05}Si_{1.95}O_6 \cdot nH_2O$ and $Na_{0.75}Al_{0.75}Si_{2.25}O_6 \cdot nH_2O$; e.g., Neuhoff et al., 2004). The stilbite–stellerite solid solution series can be ion exchanged to compositions not conforming to Mode III behavior (for instance barrerite, $Na_2Al_2Si_7O_{18} \cdot nH_2O$; Passaglia and Sacerdoti, 1982), but natural samples generally conform to the limits suggested by Passaglia et al. (1978) and Fridriksson et al. (2001; see their Fig. 1a). Low analcime is notoriously difficult to ion exchange and virtually all samples contain only Na in the extraframework sites. Extensive substitution of Na, Rb, Cs, and Ca has been observed in more disordered "high" analcimes (cf. Neuhoff et al., 2004) and the isostructural mineral pollucite (e.g., Passaglia and Sheppard, 2001). In some cases, this may reflect the original composition from which these samples crystallized, but numerous studies have demonstrated ready ion-exchange behavior between "high" analcime or pollucite and aqueous solutions (e.g., Ames, 1966; Lagache, 1995; Sebastian and Lagache, 1990).

2.4. Mode IV: independent Si–Al and extraframework cation substitution

A number of rock-forming zeolites exhibit variable Si–Al ratios and extensive extraframework cation substitutions in unmodified samples, indicating that these solid solutions are truly uncoupled in these minerals.

Examples include chabazite (Fig. 3), mordenite (Fig. 4), and the heulandite–clinoptilolite minerals (e.g., Bish and Boak, 2001). In addition, it appears that Si–Al disordering permits Mode IV behavior in some zeolites such as gonnardite (Si–Al disordered natrolite; Artioli and Galli, 1999) and high analcime (Neuhoff et al., 2004) that is otherwise not permitted in more ordered forms of the same framework structure. The extent of extraframework cation substitution may be a function of Si/Al ratio, as observed by Bish and Boak (2001) in heulandite–clinoptilolite minerals where complete solution between Ca and alkali metal cations is only possible in clinoptilolites (member of the solution series with Si/Al >4). The zeolites erionite and offretite (Passaglia et al., 1998) exhibit a variation of Mode IV behavior in which the K content is essentially constant due to its occupancy on one site within the cancrinite cage (Gualtieri et al., 1998) with Ca, Na, and Mg varying independently of Si/Al ratio.

In a strict sense, the water content of a zeolite varies independently of framework and extraframework cation contents in response to changes in temperature, pressure, and the chemical potential of H_2O (e.g., Bish and Carey, 2001; for this reason, the water contents of minerals discussed above were not explicitly specified). For given a temperature, pressure, and chemical potential of H_2O, the water content of a zeolite is typically a sensitive function of the framework and extraframework cation contents. Elucidation of the variation in water content with cation composition in zeolites is difficult to assess for several reasons. First, the water contents of some zeolites are sensitive to water vapor pressure at room temperature (e.g., laumontite; Neuhoff and Bird, 2001; Fridriksson et

Fig. 4. Compositions of natural mordenites represented in terms of the number of moles Ca versus the number of moles of Si on a 12 framework oxygen basis (Bartlett, 2002; Passaglia, 1975).

al., 2003) making comparisons between studies difficult unless humidity is controlled (which is often not the case). This can lead to difficulties in determining the true full water content (in the presence of liquid water) due to condensation/adsorption of water on zeolite powders (e.g., Carey and Bish, 1996). Second, water contents reported in the literature have been determined by a wide variety of techniques of varying precision. Lastly, modern analyses of zeolites are often performed in situ on small grains by electron probe microanalysis, which does not allow quantitative determination of true water content. Nonetheless, several general rules governing the water contents of zeolites can be elucidated.

Under ambient laboratory conditions, the available data suggest that the water content of zeolite solid solutions is sensitive to Si/Al ratio and the number and identity of extraframework cations in the structure (in many cases due to competition for space within the zeolite channels). Several generalizations can be made. First, water content tends to be inversely related to the number of extraframework cations per formula unit. This phenomenon is well-established for zeolites exhibiting substitution Modes I and III. For instance, the ordered natrolite structure minerals natrolite, mesolite, and scolecite consistently contain a total of four extraframework species (water molecules plus extraframework cations) per 10 framework oxygens; thus the Ca-bearing forms scolecite and mesolite have more water molecules per mole than does the pure Na form natrolite (e.g., Gottardi and Galli, 1985). In low analcime, water content is directly related to Si–NaAl substitution, such that at room temperature and pressure there is a substitution of $NaAlO_2$ for $SiO_2 \cdot 0.5H_2O$ (Neuhoff et al., 2004; Saha, 1959). An exception appears to be stilbite–stellerite solid solutions, in which the water
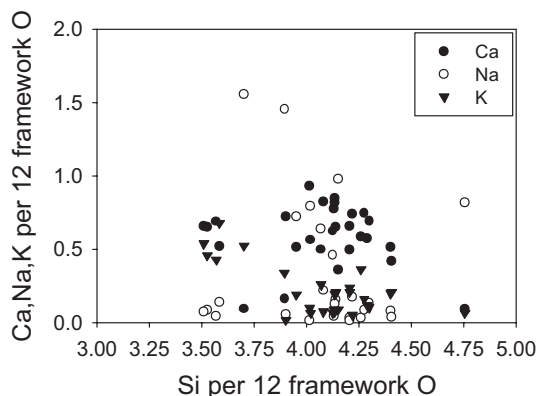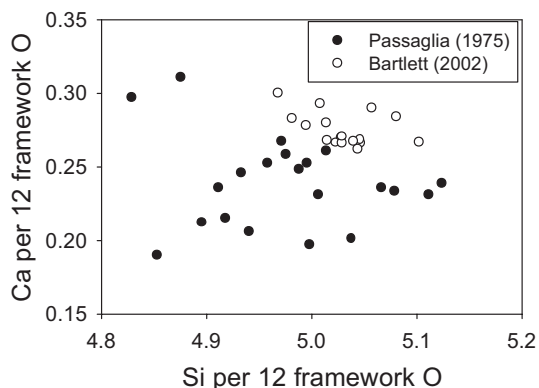

Fig. 3. Compositions of natural chabazites represented in terms of the number of moles of Na, Ca, and K versus the number of moles of Si on a 12 framework oxygen basis. Data are from the compilation of Passaglia (1970).

content increases with Na loading in the cages via a coupled substitution of $NaAlO_2 \cdot 2H_2O$ for SiO_2 (Fridriksson et al., 2001), with the additional water molecules being necessary for solvating the Na^+ ions. Second, zeolites exhibiting Mode IV substitutions either naturally or induced experimental ion exchange have variable water stoichiometries as well, both due to cation loading and cation size. For instance, substitution of large cations such at K^+ into extraframework sites often leads to reduced water content (see for example, the Na^+, Ca^{2+}, and K^+ exchanged heulandites of Fridriksson et al., 2001). An extreme example of this is provided by pollucite–analcime solid solutions, in which the water content is inversely related to Cs content because Cs occupies the water site and not the Na site in this solution (e.g., Armbruster and Gunter, 2001; Hovis et al., 2002). Outside of compositionally simple systems such as pollucite–analcime, quantitative relationships between water contents and framework and extraframework cation compositions remain elusive. Third, Mode II zeolites exhibit water contents directly related to CaAl–NaSi exchange. Fig. 5 depicts the water contents of phillipsites and thomsonites reported in the literature. In both thomsonite and the series of phillipsites that follow substitution Mode II, water content appears to decrease with increasing proportion of the Na-rich endmember. Although considerable scatter is present in the data, visual inspection suggests that the compositions reported in Fig. 5 may correspond to $CaAlO_2^+ \cdot 2H_2O$ substitution for $NaSiO_2^+$ in both minerals.

The extent of dehydration of zeolites in response to increased temperature or decreased chemical potential of H_2O is likely sensitive to both framework and extraframework cation contents. The influence of extraframework cation contents on dehydration behavior in clinoptilolite has been demonstrated both through observations of dehydration equilibria (e.g., Carey and Bish, 1996; Wilkin and Barnes, 1999) and calorimetrically determined heats of dehydration (e.g., Carey and Bish, 1997; Yang et al., 2001) for cation-exchanged forms of this mineral. Heats of dehydration determined by Shim et al. (1999) for chabazites of varying framework composition and extraframework cation contents indicate that the dehydration behavior of zeolites is sensitive to both of these factors. Elucidating the energetics of dehydration reactions as zeolite compositions vary according to Modes II, III, and IV and the variation in hydration state of these solutions as a function of temperature and pressure is an important current and future direction of research. Dehydration of zeolites is not considered in the following sections, however, as the calculations pre-
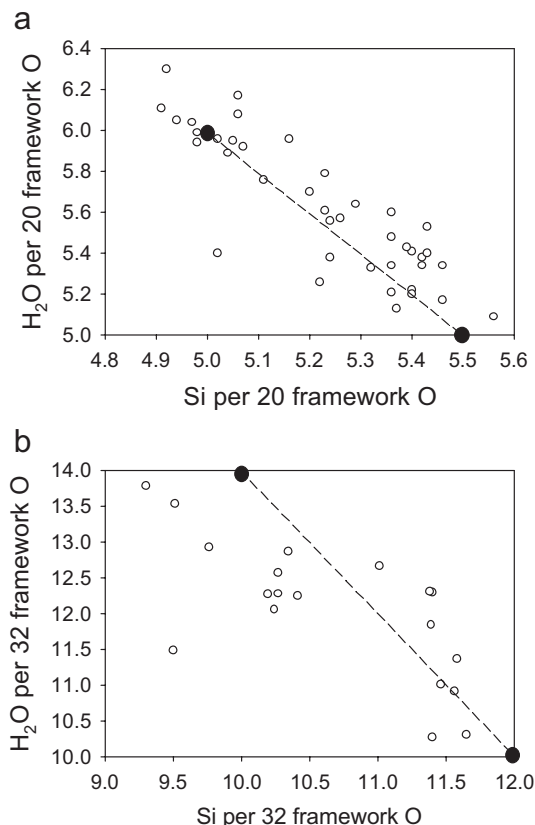

Fig. 5. Water contents of thomsonite (a) and phillipsite (b) as a function of framework content (open symbols). Data for thomsonite correspond to analyses from Hey (1932) shown in Fig. 1 and those of Galli and Ghittoni (1972) shown in Fig. 2b. The black circles and dashed lines are the endmember compositions and substitution mechanism, respectively, proposed for coupled water and Mode II substitution in these minerals.
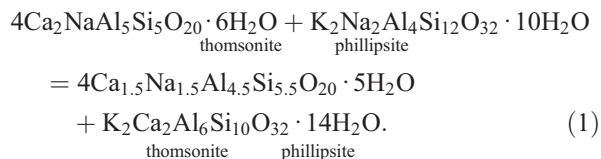
sented below pertain to water saturated conditions at relatively low temperatures. Under these conditions, the zeolite solid solutions considered below likely experience little dehydration relative to their water contents under laboratory conditions (Neuhoff, 2000).

3. Reactions buffering zeolite composition in nature

The variable chemistry of many rock-forming zeolites suggests that critical analysis of the mechanisms and thermodynamics of solid solution in these phases may provide a means to use zeolite composition in natural systems as a monitor of intensive variables such as temperature, pressure, and chemical potentials. In the case of zeolites that exhibit Mode I behavior, considerable work has already been undertaken to investigate univariant phase equilibria governing the stability of theses phases as a function of temperature and pressure (e.g., Liou, 1970, 1971b; Zeng and Liou, 1982). Analy-

sis of reported phase equilibria involving zeolites that exhibit substitutions following Modes III and IV (e.g., stilbite, analcime, and heulandite; Liou, 1971a,c; Cho et al., 1987; Thompson, 1970, 1971) necessarily requires consideration of the effects of solid solution on the positions of experimentally determined univariant curve; these effects are likely the source of reported inconsistencies between reported equilibria (e.g., see Neuhoff, 2000; Fridriksson et al., 2001; Neuhoff et al., 2003; Thompson, 1973). If thermodynamic models of these solid solutions can be defined, then there is potential for the use of equilibria involving these minerals as geothermobarometers and monitors of chemical potential in geologic systems. Potential reactions governing the stability and composition of zeolites exhibiting substitution Modes II through IV and their chemographic consequences are considered below.

Reactions controlling the stability and composition of zeolites exhibiting Mode II behavior likely involve other zeolites or feldspars or heterogeneous equilibrium with aqueous species. For instance, equilibrium between coexisting thomsonite and phillipsite in very low-grade metabasalts (e.g., Neuhoff et al., 1997) might be described by the reaction
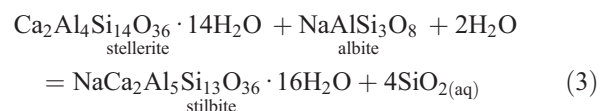
$$4Ca_2NaAl_5Si_5O_{20} \cdot 6H_2O + K_2Na_2Al_4Si_{12}O_{32} \cdot 10H_2O$$
$$\underset{\text{thomsonite}}{} \quad \underset{\text{phillipsite}}{}$$
$$= 4Ca_{1.5}Na_{1.5}Al_{4.5}Si_{5.5}O_{20} \cdot 5H_2O$$
$$+ K_2Ca_2Al_6Si_{10}O_{32} \cdot 14H_2O. \qquad (1)$$
$$\underset{\text{thomsonite}}{} \qquad \underset{\text{phillipsite}}{}$$

Another potential equilibrium relation governing the composition of thomsonite coexisting with analcime (here represented by the idealized formula NaAl-Si$_2$O$_6$·H$_2$O), scolecite, and dissolved silica in an aqueous solution in very low-grade metabasalts is

$$Ca_2NaAl_5Si_5O_{20} \cdot 6H_2O + 0.5NaAlSi_2O_6 \cdot H_2O$$
$$\underset{\text{thomsonite}}{} \qquad \underset{\text{analcime}}{}$$
$$+ 2SiO_{2(aq)}$$
$$= Ca_{1.5}Na_{1.5}Al_{4.5}Si_{5.5}O_{20} \cdot 5H_2O$$
$$\underset{\text{thomsonite}}{}$$
$$+ 0.5CaAl_2Si_3O_{10} \cdot 3H_2O. \qquad (2)$$
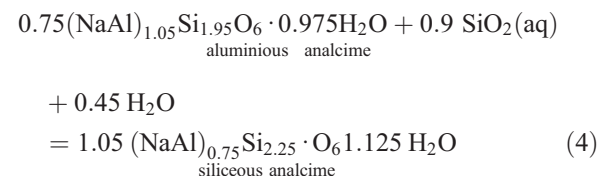$$\underset{\text{scolecite}}{}$$
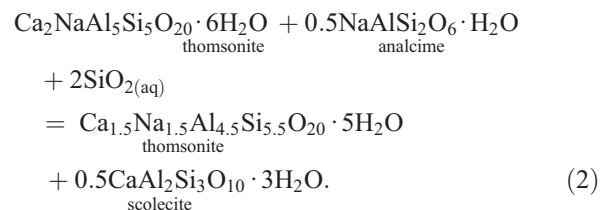
Analcime occurs at lower metamorphic grades than scolecite, and the form of reaction (2) is generally consistent with the tendency for thomsonite to exhibit compositions that progressively approach the Na,Si-rich endmember with increasing grade in zeolite facies basalts in eastern Iceland (Neuhoff, unpublished data). Unfortunately, the thermodynamic consequences of Mode II substitutions in zeolites have not been inves-

tigated, precluding quantitative modeling of the equilibria suggested above.

Zeolites exhibiting Modes III and IV substitutions both exhibit substitutions involving an exchange of a $SiO_2 \cdot nH_2O$ component for a cation-AlO_2 component (e.g., NaAlO$_2$). Consequently, equilibria governing the composition of these zeolites in natural systems can be expressed in terms of chemical equations involving only endmembers in these solid solutions, water, other stoichiometric minerals, and either solid or dissolved silica. For instance, the equilibrium compositions of the Mode III minerals stilbite and analcime can be expressed by the chemical equations

$$Ca_2Al_4Si_{14}O_{36} \cdot 14H_2O + NaAlSi_3O_8 + 2H_2O$$
$$\underset{\text{stellerite}}{} \qquad \underset{\text{albite}}{}$$
$$= NaCa_2Al_5Si_{13}O_{36} \cdot 16H_2O + 4SiO_{2(aq)} \qquad (3)$$
$$\underset{\text{stilbite}}{}$$

and

$$0.75(NaAl)_{1.05}Si_{1.95}O_6 \cdot 0.975H_2O + 0.9 \ SiO_2(aq)$$
$$\underset{\text{aluminious \ analcime}}{}$$
$$+ 0.45 \ H_2O$$
$$= 1.05 \ (NaAl)_{0.75}Si_{2.25} \cdot O_6 1.125 \ H_2O \qquad (4)$$
$$\underset{\text{siliceous \ analcime}}{}$$

for which the corresponding equilibrium constant (K) expressions can be expressed (assuming unit activity of water) as
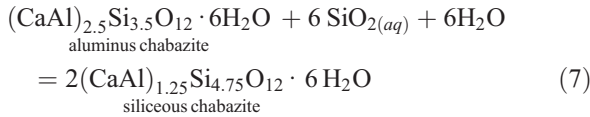
$$\log K_{(3)} = 2 \log a_{SiO_{2(aq)}} + \log a_{stilbite} - \log a_{stellerite} \quad (5)$$

and

$$\log K_{(4)} = 1.05 \log a_{siliceous \ analcime}$$
$$- 0.75 \log a_{aluminous \ analcime} - 0.9 \log a_{SiO_{2(aq)}}$$
$$(6)$$

where a_i corresponds to the activity of species i. Inspection of Eqs. (5) and (6) shows that the composition of stilbite and analcime is thus expressed solely as a function of K (which is a function of temperature and pressure) and the chemical potential of SiO$_2$ in the system, here represented by the activity of aqueous silica. For zeolites exhibiting Mode IV substitutions, solid solution on the extraframework sites is uncoupled from solid solution within the tetrahedral framework (although the energetics of ion exchange is affected by framework composition; see Shibue, 1981; Fridriksson et al., 2004). In these minerals, the Si/Al ratio can be related directly to the chemical potential of SiO$_2$. One approach is to establish homoionic endmembers representing the range of Si and Al substitution in the framework. For instance, in the case of chabazite, one

could represent such a relation for homoionic Ca-end-members via the chemical equation

$$
\underset{\text{aluminus chabazite}}{(CaAl)_{2.5}Si_{3.5}O_{12} \cdot 6H_2O} + 6\ SiO_{2(aq)} + 6H_2O
$$
$$
= \underset{\text{siliceous chabazite}}{2(CaAl)_{1.25}Si_{4.75}O_{12} \cdot 6\ H_2O} \tag{7}
$$

for which the equilibrium constant expression would be

$$
\log K_{(7)} = 2 \log a_{\text{siliceous chabazite}}
$$
$$
- \log a_{\text{aluminous chabazite}} - 2 \log a_{SiO_{2(aq)}}. \tag{8}
$$

An alternative approach is to adopt a hypothetical pure silica endmember. Purely siliceous zeolites, although not known in nature, have been synthesized for a number of zeolite structure types, including chabazite (Woodcock et al., 1999). Using this approach, the chemical equation is

$$
SiO_{2(chabazite)} = SiO_{2(aq)} \tag{9}
$$

and the corresponding equilibrium constant expression is given by

$$
\log K_{(9)} = \log a_{SiO_{2(aq)}} - \log a_{SiO_{2(chabazite)}} \tag{10}
$$

In the case of chabazite, the thermodynamic properties of reaction (9) can be evaluated more rigorously than those of reaction (7), and this approach is used in the calculations described below.

4. Thermodynamic properties of SiO_2 exchange vectors in zeolites

Recent experimental emphasis on the thermodynamic and structural properties of zeolites provides a basis for evaluating the energetics of Si–Al substitution in zeolites exhibiting Mode III and IV behavior. The relationship between composition and activity in solid solutions is usually described in terms of the excess Gibbs energy of mixing (G^{EX}) in the solutions, given by

$$
G^{EX} = H^{EX} - TS^{EX} \tag{11}
$$

where H^{EX} and S^{EX} are the excess enthalpy and entropy of mixing, respectively. The activity of an endmember k in a solid solution is the product of its mole fraction (X_k) and the activity coefficient γ_k, given by the relation

$$
RT\ln\gamma_k = G^{EX} - (1 - X_k)\big(\partial G^{EX} / \partial(1 - X_k)\big)_{T,P,X_k}. \tag{12}
$$

Recent calorimetric data combined with theoretical advances in the interpretation of diffraction and spec-troscopic data now allow explicit evaluation of the excess mixing functions and thus activity composition relations. Key insights from these studies are reviewed here and applied below to describe the composition and paragenesis of zeolites in natural systems.

Several recent studies have concluded that H^{EX} is negligible for Si–Al substitution via Modes III and IV. Calorimetric determinations of the enthalpy of formation (ΔH_f) as a function of Si and Al content for the Mode III zeolite analcime (Neuhoff et al., 2004; Barany, 1962; Johnson et al., 1982) and Mode IV zeolites faujasite (Petrovic et al., 1993; Petrovic and Navrotsky, 1997; Yang and Navrotsky, 2000) and chabazite (Shim et al., 1999) are all linear with respect to the number of moles of Si per formula unit. The partial molar enthalpies of formation of the SiO_2 component calculated from these studies is consistent with determinations of ΔH_f for pure SiO_2 zeolites, being ~6–15 kJ/mol less stable than quartz (Piccione et al., 2000). In addition, Fridriksson et al. (2001) found that geologic and experimental observations of phase equilibria involving stilbite–stellerite solid solutions could only be explained by assuming negligible heats of mixing. As a consequence of these relations, the H^{EX} term in Eq. (11) can be ignored and Mode III and IV solutions are thus athermal solutions (γ_k is not a function of temperature).

Although H^{EX} is negligible for Mode III and IV substitutions in zeolites, these solutions are not ideal due to the presence of short- and long-range Si–Al ordering due to Al avoidance (the absence of Al–O–Al linkages in the framework; Loewenstein, 1954). Estimates of Si and Al site occupancies in zeolites from published crystal structures (Alberti, 1991) demonstrate distinctly non-random Si and Al occupancies among sites that are regular functions of Si/Al ratio. In zeolite structures that do not contain multiple, crystallographically distinct tetrahedral sites (e.g., faujasite, zeolite A, chabazite, analcime), ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) data clearly demonstrate that short-range ordering exists in order to maintain Al avoidance (e.g., Phillips and Kirkpatrick, 1994; Neuhoff et al., 2003). Consequently, the configurational entropy (S_{CON}) arising from the distribution of Si and Al within zeolite structures is lower than for the fully disordered case, leading to finite, negative values for S^{EX} and thus positive values for G^{EX} from Eq. (11) (Neuhoff and Stebbins, 2001). Calculation of S_{CON} arising from Si–Al occupancies from crystal structures or ^{29}Si MAS NMR data as a function of composition allows for explicit evaluation of S^{EX} and thus the relationship between activity and

composition via Eqs. (11) and (12) (Neuhoff and Stebbins, 2001; Neuhoff et al., 2003, 2004). An alternative approach was employed by Fridriksson et al. (2001), in which the compositional dependence of S^{EX} was described by an empirical Margules parameter fit to experimental and geologic equilibrium observations.

5. Thermodynamic methods

In order to demonstrate the effects of temperature, pressure, and the chemical potential of SiO_2 on the composition of stilbite–stellerite, analcime, and chabazite solid solutions, thermodynamic calculations were conducted with the aid of the computer code SUPCRT92 and its associated thermodynamic database (Johnson et al., 1992). Consistent with the conventions employed in SUPCRT92, the standard states adopted in the present study for pure minerals and mineral endmembers and liquid water correspond to unit activity of the pure phase at all temperatures and pressures. The standard state for aqueous species is unit activity at all temperatures and pressures of a hypothetical one molal solution referenced to infinite dilution. Thermodynamic properties for albite (in its stable state of Si–Al order–disorder at all temperatures and pressures; cf. Helgeson et al., 1978), silica polymorphs, water, and aqueous species included in SUPCRT92 were adopted for the calculations. The thermodynamic properties of endmembers in the stilbite–stellerite and low analcime solid solutions, and well as solution models describing the properties of mixing in these solutions, were taken from Fridriksson et al. (2001) and Neuhoff et al. (2004), respectively.

Several calorimetric studies of the thermodynamic properties of chabazite solid solutions have been conducted (e.g., Shim et al., 1999; Belitsky et al., 1982; Petrova, 1997; Drebushchak, 1990; Ogorodova et al., 2002); nonetheless, there are still insufficient data to derive reliable properties of homoionic endmembers such as those depicted in Eq. (7). This is due to insufficient characterization of the effect of composition on those properties and large errors on calorimetrically derived enthalpies of formation (ΔH_f). Consequently, the thermodynamic properties of these solutions were modeled using the approach of reaction (9). Note that in reaction (9) the presence of water in chabazite is not taken into account. There are two reasons for this: first, the water content of chabazite is variable, but apparently is not strongly dependent on framework composition (Passaglia, 1970); and second, the partial molal properties of water in pure silica zeolite endmembers are energetically similar to liquid water (Neuhoff et al.,

2004) and thus have a negligible effect on the properties of reaction (9).

Neuhoff et al. (2003) derived an athermal solution model to describe the properties of mixing among tetrahedral sites in chabazite based on values of S^{EX} calculated from ^{29}Si MAS NMR data. This model is adopted here and modified for the single tetrahedral site stoichiometry shown in reaction (9). Using the regressions and equations of Neuhoff et al. (2003), and adjusting to a one tetrahedral site basis, the activity of $SiO_{2(chabazite)}$ is related to its mole fraction ($X_{SiO_{2(chabazite)}}$) by the relationship

$$a_{SiO_{2(chabazite)}} = \left(X_{SiO_{2(chabazite)}} \right)^{(4.667/R)} \tag{13}$$

where the gas constant (R) is in units of J/mol K.

The thermodynamic properties of $SiO_{2(chabazite)}$ were assessed from experimental measurements on this phase and the pure silica form of the closely related zeolite faujasite. Piccione et al. (2000) determined ΔH_f of anhydrous $SiO_{2(chabazite)}$ relative to that of quartz and other silica polymorphs through lead borate solution calorimetry. The resulting value of ΔH_f (taken to be the standard state value at 298.15 K, 1 bar, ΔH_f°) for $SiO_{2(chabazite)}$ is -899.5 kJ/mol. Woodcock et al. (1999) reported the standard molal volume of $SiO_{2(chabazite)}$ at 298.15 K, 1 bar to be 39.1 cm^3/mol. No experimental determinations of the heat capacity (C_p) of $SiO_{2(chabazite)}$ are available. However, Boerio-Goates et al. (2002) measured C_p of pure silica faujasite over the temperature range 14.6 to 398.9 K. Because of the structural similarities between chabazite and faujasite (the structures of both are composed of the same fundamental building block, the double six ring; Meier et al., 2001), the C_p measurements of Boerio-Goates et al. (2002) were used to approximate those of chabazite. The resulting standard molal Third law entropy at 298.15 K, 1 bar (S°) is 44.73 kJ/mol K, and the temperature dependence of the standard molal heat capacity (C_p°) is given by the equation

$$C_p^\circ (J/molK) = 19.48 + 87.61\,T, \tag{14}$$

where T is the temperature in K. Errors arising from this approximation are probably minimal (<200 J/mol SiO_2) as the observed variations in C_p° and S° between zeolitic pure silica polymorphs are only on the order of 2.5 and 1.0 cal/mol K, respectively. The standard Gibbs energy of formation at 298.15 K, 1 bar (ΔG_f°) for $SiO_{2(chabazite)}$ (calculated from the values of S° and ΔH_f° listed above, and those of the elements from Wagman et al., 1968) is -846.1 kJ/mol.

6. Implications for interpretation of natural zeolite parageneses

The presence of $SiO_2 \cdot nH_2O$ exchange vectors in zeolites exhibiting Mode III and IV substitutions suggests that the Si/Al ratio in these materials should reflect the chemical potential of SiO_2 during their formation. This is well known in the synthesis of zeolites such as faujasite that exhibit Mode IV substitution, where the Si/Al ratio of synthesized zeolites is a sensitive function of the batch composition of the starting gels (Lechert, 2000). In turn, the compositions of Modes III and IV zeolites may actually buffer SiO_2 activities in natural and experimental systems.

Figs. 6, 7, and 8 show the equilibrium compositions of stilbite, analcime, and chabazite, respectively as a function of temperature and $a_{SiO_{2(aq)}}$ at pressures corresponding to liquid–vapor saturation for pure water. The isopleths of mineral composition (dashed curves) in these figures were calculated from the properties of reactions (3), (4), and (9). The activity of water was taken to be unity. Shown for reference in these diagrams is the temperature dependence of $a_{SiO_{2(aq)}}$ in equilibrium with quartz, cristobalite, and amorphous silica. In each case, it can be seen that the Si/Al ratio in the zeolite is a sensitive function of $a_{SiO_{2(aq)}}$.

In Fig. 6 it can be seen that the composition of stilbite–stellerite solid solutions is sensitive to temperature at all silica activities. Stilbite commonly coexists with quartz in zeolite facies metabasalts, and inspection of Fig. 6 indicates that stilbite–stellerite solid solutions should become progressively less NaAl-rich with in-

Fig. 7. Composition of analcime (dashed curves) as a function of temperature and the activity of aqueous silica at pressures corresponding to liquid–vapor equilibrium for pure water (P_{SAT}). Solid curves show the activity of aqueous silica in equilibrium with quartz, cristobalite, and amorphous silica. The leftmost gray box denotes the temperature of occurrence (Kristmannsdóttir and Tómasson, 1978) and compositions of analcime in zeolite facies metabasalts in Iceland (Neuhoff, unpublished data) and the rightmost gray box denotes the temperatures and compositions of neo-formed analcime in diagenetically altered tuffs in Japan (Iijima, 1988).

creasing temperature at quartz equilibrium. This is exactly what is observed in both geothermal systems and regional metamorphic terrains (Fridriksson et al., 2001). The relatively shallow slopes of the compositional isopleths for stilbite–stellerite solutions compared to the silica polymorph solubilities in Fig. 6 is a consequence of the partial molar enthalpy of formation for SiO_2 in stilbite being more positive (less stable) than ΔH_f of even amorphous silica.
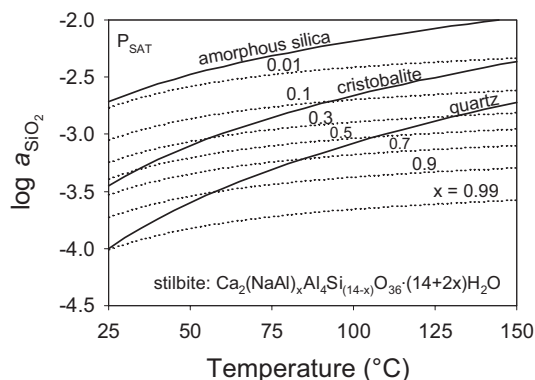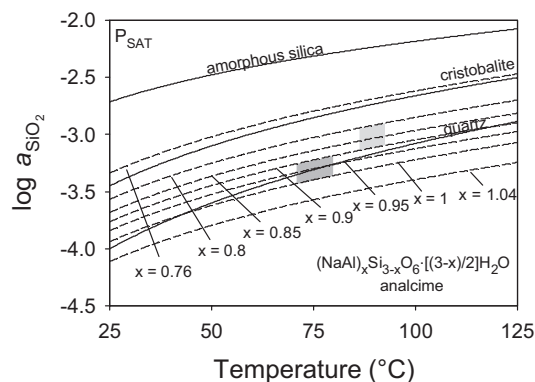

Fig. 6. Composition of stilbite–stellerite solid solutions (dashed curves) in equilibrium with albite as a function of temperature and the activity of aqueous silica at pressures corresponding to liquid–vapor equilibrium for pure water (P_{SAT}). Solid curves show the activity of aqueous silica in equilibrium with quartz, cristobalite, and amorphous silica.
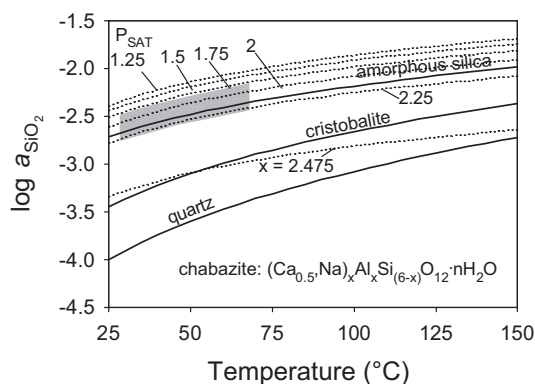

Fig. 8. Composition of chabazite (dashed curves) as a function of temperature and the activity of aqueous silica at pressures corresponding to liquid–vapor equilibrium for pure water (P_{SAT}). Solid curves show the activity of aqueous silica in equilibrium with quartz, cristobalite, and amorphous silica. The gray box denotes the temperature of occurrence (Kristmannsdóttir and Tómasson, 1978) and compositions of chabazite in zeolite facies metabasalts in Iceland (Neuhoff, unpublished data).

The composition of analcime is also sensitive to temperature at quartz saturation but is not a function of temperature at cristobalite saturation (Fig. 7). This is a direct consequence of the fact that the partial molar enthalpy of SiO_2 in analcime is very similar to ΔH_f of cristobalite (Neuhoff et al., 2004). The compositions of analcime predicted by these compositions appear to be consistent with observations in natural systems. The solid gray box in Fig. 7 shows the temperature of formation (Smárason et al., 1989) and compositions (Neuhoff, unpublished data) of analcime from zeolite facies metabasalts in Iceland. The silica activities corresponding to this field are consistent with quartz saturation. Silica polymorphs are typically not observed coexisting with analcime in these rocks, but reported fluid compositions from geothermal systems in Iceland (Gíslason and Arnórsson, 1990) are typically slightly supersaturated with respect to quartz at these temperatures. The hatched gray box in Fig. 7 shows the temperatures of formation and compositions of analcime in tuffaceous sediments undergoing active diagenesis in Japan (Iijima, 1988). Formation of analcime in these systems is accompanied by a transition in silica mineralogy from cristobalite to quartz (see also Chipera and Bish, 1997; Hay, 1966; Smyth, 1982); $a_{SiO_{2(aq)}}$ predicted from analcime compositions in these sediments is consistent with this transition.

Chabazite compositions (Neuhoff, unpublished data) observed in zeolite facies metabasalts altered at temperatures between 30 and 70 °C (cf. Kristmannsdóttir and Tómasson, 1978) in Iceland are denoted in Fig. 8 by the gray box. The corresponding values of $a_{SiO_{2(aq)}}$ are consistent with amorphous silica saturation; indeed, chabazite and opaline silica commonly coexist in these rocks (Neuhoff et al., 1999). The framework composition of chabazite is not strongly dependent on temperature at amorphous silica saturation but does become more silica-rich with increasing temperature at cristobalite and quartz saturation. This relationship reflects the similar value of ΔH_f for $SiO_{2(chabazite)}$ (Piccione et al., 2000) and amorphous silica (Helgeson et al., 1978) that is more positive (less stable) than that of quartz and cristobalite. Note that ΔH_f° and ΔG_f° for $SiO_{2(chabazite)}$ used in the present study were derived from calorimetric data, and are generally not as precise as the phase equilibrium constrained data used to construct Figs. 6 and 7 (cf. Helgeson et al., 1978). The standard error in ΔH_f° calculated from the results reported by Piccione et al. (2000) is 1 kJ/mol, which corresponds to a maximum error (at 25 °C) in the position of the isopleths at any given temperature of $\sim 0.2 \log a_{SiO_{2(aq)}}$.

The temperature dependence of the composition of stilbite–stellerite, analcime, and chabazite solid solutions at conditions buffered by the presence of silica polymorphs potentially provides a means of performing thermobarometric calculations in diagenetic and very low grade metamorphic systems. If a silica polymorph is substituted for $SiO_{2(aq)}$ in chemical Eqs. (3), (4), and (9), then the phase assemblages become divariant. For instance, the assemblage in Eq. (3) can be described by four thermodynamic components ($Ca_{0.5}AlO_2$, $NaAlO_2$, SiO_2, and H_2O) and there would be four phases (stilbite–stellerite solution, albite, silica polymorph, and the fluid) resulting in two degrees of freedom via the phase rule. This allows calculation of discrete isopleths of mineral composition as a function of temperature and pressure.

An example is shown in Fig. 9, in which the composition of chabazite in equilibrium with cristobalite is plotted as a function of temperature and pressure. Similar diagrams have been constructed for stilbite (Fridriksson et al., 2001) and analcime (Neuhoff et al., 2004). In the case of chabazite depicted in Fig. 9, the composition of this mineral in equilibrium with cristobalite varies slightly (between ~ 2.4 and ~ 2.5 Al per 24 framework O over the pressure and temperature range of Fig. 9) with temperature and pressure, with high pressures/low temperatures favoring more Al-rich compositions. This small dependence of framework composition on temperature and pressure is a consequence of the relatively small enthalpy and volume differences between cristobalite and pure silica chabazite. This underscores a central difficulty in developing thermobarometers for low temperature systems: the geochemical reactions governing mineral stability under these conditions often have relatively small energy changes associated with them. The quartz analogs of reactions (3) and (4) describing solid
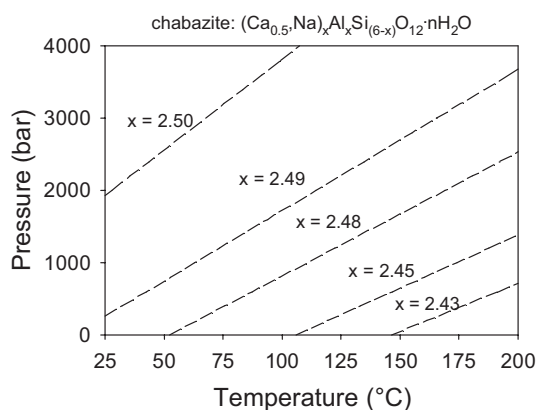

Fig. 9. Composition of chabazite in equilibrium with cristobalite as a function of temperature and pressure.

solution in stilbite and analcime, respectively, have enthalpies of reaction that are ~9 and ~5 times larger, respectively, than the enthalpy of reaction for the cristobalite analog of reaction (9). This leads to a much greater dependence of composition on temperature (although the pressure dependence is lower due to smaller volumes of reaction). Because of the relatively large enthalpy change across the quartz analog of reaction (2), the stilbite solid solution–albite–quartz thermometer the most robust zeolite facies thermobarometric system explored to date. Nonetheless, the compositions of chabazite, analcime, and stilbite–stellerite solid solutions are all useful monitors of the chemical potential of silica.

7. Conclusions

Apart from zeolites that do not exhibit appreciable Si/Al substitution and a few cases in which coupled CaAl–NaSi exchange exists, most rock-forming zeolite solid solutions involve $SiO_2 \cdot nH_2O$ compositional exchange vectors. Calorimetric data and structural interpretations now available for assessing the thermodynamic properties of mixing along these exchange vectors all point to these solutions behaving athermally. Where calorimetric and phase equilibrium data necessary to evaluate the stability of these solid solutions exist, thermodynamic calculations of the composition of these minerals in natural systems as a function of temperature, pressure, and the chemical potential of SiO_2 promise to be an important tool for interpreting conditions attending diagenesis and very low grade metamorphism. The successful application of these principles to the interpretation of stilbite-, analcime-, and chabazite-bearing mineral parageneses underscores the need for further study of the crystal chemistry and thermodynamics of these common rock-forming minerals and their solid solutions.

Acknowledgements

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