Chemical Geology xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

The system $MgO-Al_2O_3-SiO_2$ under pressure: A computational study of melting relations and phase diagrams

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ARTICLE INFO

Article history:
Received 26 February 2016
Received in revised form 18 October 2016
Accepted 9 November 2016
Available online xxxx

Keywords:
MAS system
Melting
Thermodynamics
First principles
Phase diagram
High pressure

ABSTRACT

A computational scheme to predict melting phase relations in multi-component systems at high pressure and temperature is presented and applied to the $MgO-Al_2O_3-SiO_2$ (MAS) compositional system. A combined approach based on first principles calculations (hybrid DFT and Polarized Continuum Model), polymer chemistry (Hybrid Polymeric Approach, HPA) and equilibrium thermodynamics is developed to compute thermophysical and thermodynamic properties of the solid and liquid phases in the investigated system and infer the liquidus topology of binary and ternary phase diagrams in a broad range of P-T conditions (i.e. up to 25 GPa and 5000 K). The nature of ternary interactions in the liquid is discussed in terms of an excess Gibbs free energy contribution arising from the effect of polarization of charged species in the continuum. The computed phase diagrams show that pressure effects are able to change the nature of melting from congruent to incongruent and drastically reduce the number of solid phases with a primary phase field in the MAS system, thus leading to a remarkable simplication of melting phase relations at HP-HT. At pressures >2 GPa a primary phase field of pyrope garnet opens and progressively widens from 2 to 8 GPa at the expense of those of enstatite, forsterite and spinel. Anhydrous phase B (AnhB) completely replaces forsterite on the liquidus at 9 GPa, persisting as stable liquidus phase at least up to 16–17 GPa and 2700–2750 K. At P-T conditions compatible with the mantle transition zone, the MAS phase diagram markedly simplifies, with the three pure oxides (i.e. MgO, periclase; Al_2O_3, corundum; SiO_2, stishovite) displaying a primary phase field and majorite-pyrope garnet as the only, and most important, ternary liquidus phase in the system.

1. Introduction

Understanding melting phase relations in complex geological systems is hindered by a still lacking knowledge of the thermodynamic properties of liquid and solid phases at high pressures and temperatures (HP-HT). Laboratory measurements can be applied to complex compositions and roughly constrain the onset of melting at HP-HT conditions, but they usually suffer from large uncertainties (mainly due to high thermal gradients) and rarely predict the ultimate nature of melting. Atomistic simulations (e.g. ab initio or semi-empirical molecular dynamics) give useful insights on the structure-energy properties of solid and liquid phases up to very HP-HT conditions, but provide contradictory results on melting even for simple solids, like MgO (Belonoshko et al., 2010) and their application to multi-component systems is still complicated and limited by computational cost. Other empirical methods (e.g. the Lindemann criterion) can be useful to fit experimental data but, in general, are not adequate to describe the melting behaviour of minerals as they do not have a predictive power (Wolf and Jeanloz, 1984). As a matter of fact, the interpretation of melting processes at HP-HT conditions is, at present, highly speculative.

In this context, a thermodynamically-consistent computational framework is developed to predict melting phase relations in multi-component systems at high pressures and temperatures by using a combination of well-established theoretical methods (briefly described in Section 2). These methods basically provide the Gibbs free energy values of all the solid and liquid phases within a given compositional system on a grid of P-T-X conditions and allow to infer melting phase relations by minimisation algorithms. The $MgO-Al_2O_3-SiO_2$ (MAS) system has been chosen to test our model calculations for several reasons. First of all, this system is particularly relevant at HP-HT conditions as it accounts for ~90% of a pyrolite bulk composition (Irifune, 1987), being so a realistic proxy for a deep mantle system. Adding further chemical components to the system is expected to modify but not qualitatively change melting relations at HP-HT (Gasparik, 2000, 2014). High-pressure melting relations in the MAS system provide also important clues on the generation, differentiation and crystallization behaviour of basaltic magmas and deep magma oceans in the Earth's interior (Presnall et

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http://dx.doi.org/10.1016/j.chemgeo.2016.11.011
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al., 1998). Finally, MAS is a reference model system to develop high-temperature refractory ceramics and metallurgical slags (Jung et al., 2004).

High-pressure and high-temperature phase relations in MAS system have been extensively investigated at sub-solidus conditions (e.g. Schreyer and Seifert, 1969; Gasparik, 1994). There are also studies on melting relations at 1-bar pressure, based both on experimental measurements (Rankin and Merwin, 1918; Foster, 1950; Keith and Schairer, 1952; Smart and Glasser, 1976) and thermodynamic assessments (Jung et al., 2004; Mao et al., 2005a). Nevertheless, investigations on liquidus phase relations at HP-HT conditions are limited to the relatively low-pressure range (Taylor, 1973; Milholland and Presnall, 1998; Liu and Presnall, 2000) or to sub-systems (Gasparik, 1992; Kudo and Ito, 1996). In this work we extend the thermodynamic investigation of melting relations in the MAS system to conditions relevant to a deep mantle environment (i.e. 25 GPa and 5000 K), relying on a selected dataset of computed thermodynamic and thermophysical properties of solid and liquid phases, as discussed in Section 3. The calculated phase diagrams are then used as source of information to gain new insights on the stability at liquidus of minerals up to P-T conditions compatible with the mantle transition zone (i.e. up to ~660–700 km depths).

2. Theory and calculation method

An integrated theoretical and computational approach based on first principles calculations, polymer chemistry and equilibrium thermodynamics has been developed to obtain melting phase relations in multi-component systems at HP-HT. Phase diagram topology is computed in a wide range of P-T conditions by a Gibbs free energy minimisation algorithm which employs the convex-hull method to analyze equipotential surfaces in multi-component systems. The convex-hull technique is described elsewhere (e.g. Attene and Ottonello, 2011; Natali et al., 2013; Ottonello et al., 2013), while some examples on the use of this method to calculate ternary phase diagrams can be found in the literature (e.g. Connolly and Kerrick, 1987; Voskov and Voronin, 2010; Voskov et al., 2015).

Heat capacity (C_P), standard-state entropy ($S^0_{298.15}$) and enthalpy of formation from the elements ($H^0_{f,298.15}$) of the pure liquid end-member compositions (i.e. MgO, Al_2O_3 and SiO_2) have been obtained from ab initio structure-energy and vibrational calculations performed with the Polarized Continuum Model (PCM) (Tomasi and Persico, 1994; Ottonello et al., 2010a; Belmonte et al., 2013; see also Supplementary material for details). Thermophysical properties and equation-of-state parameters of the pure liquid components have been assessed in order to be consistent with the observed melting curves at HP-HT conditions (see Section 3.1).

The Gibbs free energy of mixing (G_{mixing}) of multi-component liquids is obtained via the Hybrid Polymeric Approach (HPA; Ottonello, 2005) as a sum of discrete contributions arising from different kinds of interaction among chemical species in the structure of a polymeric substance. The different energy terms are represented by a dominant chemical interaction taking place among polymeric units (structons), a subordinated interaction taking place in the cation matrix and a strain energy contribution arising from medium-range disorder of the various structons within the anion matrix, i.e.:

$$G_{mixing} = G_{chemical} + G_{cat.mix\text{-}id} + G_{cat.mix\text{-}exc} + G_{strain} \tag{1}$$

Since the liquid compositions investigated in this study have only one basic oxide in the cation matrix (i.e. MgO), the second and third terms on the right-hand side of Eq. (1) are equal to zero and can be disregarded in the following. The chemical interaction between network formers (NF) and network modifiers (NM) constitutes by far the main form of energy gained (or lost) by the liquid in the mixing process. This energy can be expressed according to the Toop-Samis model (Toop and Samis, 1962a, 1962b) as:

$$G_{chemical} = \frac{(O^-)}{2} RT\ln K_P \tag{2}$$

where $(O^-)/2$ (i.e. half the concentration of non-bridging oxygens in the melt structure) defines the number of contacts among the functionals of the polymeric units and K_P is the polymerization constant that describes the chemical energy acquired by the melt in a single interaction among different types of oxygen, i.e.:

$$K_P = \frac{\left(O^{2-}\right) \times \left(O^0\right)}{\left(O^-\right)^2} \tag{3}$$

where O^{2-} are free oxygens, O^0 bridging oxygens and O^- non-bridging oxygens. In the HPA model the polymerization constant can be expressed as:

$$\ln K_P = {}^{A}\!/_{T} + B \tag{4}$$

The A and B coefficients in Eq. (4) acquire a precise thermodynamic meaning since they represent the enthalpic and entropic contributions to the chemical interaction energy between NF and NM per unit mole of contacts (see Section 3.2 for further details).

If the effects of the direct interaction between network formers in the anion matrix (weighted on their fractional amount in the system) are added to the NF-NM chemical interaction along with an excess energy term related to the electrostatic interactions of the NM sub-lattice, we have:

$$G_{chemical} = \frac{(O^-)}{2} RT\ln K_P + \left[\frac{(O^-)^*}{2} RT\ln K_{IJ}\right]\left(\frac{X_{NF}}{X_{NF} + X_{NM}}\right) + G_{excess} \tag{5}$$

where X_{NF} and X_{NM} are the molar fractions of network formers and modifiers, respectively, $(O^-)^*$ is the molar amount of non-bridging oxygen involved in NF-NF interactions and K_{IJ} is the equilibrium constant defined for the Ith and Jth network-forming oxide species (i.e. Al_2O_3 and SiO_2 in the MAS system). The last term in Eq. (5) (i.e. G_{excess}) will be defined and discussed in detail in Section 3.3 as it deserves particular attention.

The Hookean strain energy contribution to G_{mixing} (i.e. G_{strain} in Eq. (1)) represents the energy spent (or gained) in conforming the relative arrangement of the various polymers in the anion sub-lattice. This term is defined by following the same combinatory rules for network formers and network modifiers (Ottonello, 2005), i.e.:

$$G_{strain} = \frac{(O^-)}{2} T\eta + \left[\frac{(O^-)^*}{2} T\eta^*\right]\left(\frac{X_{NF}}{X_{NF} + X_{NM}}\right) \tag{6}$$

$$\eta = \sum_{k=0}^{n} \eta_k \cdot (2X_{NF} - 1)^k \tag{7}$$

$$\eta_0 = \eta_{0,H} - \eta_{0,S} \times T + \eta_{0,V} \times P \tag{8}$$

The procedure to obtain the strain coefficients (η and η^* in Eqs. 6–8) can be defined as an *asymmetric* Toop deconvolution because values of K_P are constant along pseudo-binaries with fixed $SiO_2/(SiO_2 + Al_2O_3)$ ratio. Moreover, the interactions within the cation and anion sub-lattices are mutually unaffected with respect to each other. Calculations for the MAS system are rather simple because mixing terms in the cation matrix are absent and the phase topology is simply dictated by the contrasting Lux-Flood behaviour (Lux, 1939; Flood and Förland, 1947) of the three oxide components (i.e. the liquidus surface at 1-bar pressure is satisfactorily conformed by nine A-B-η coefficients plus the ternary electrostatic excess polarization; see Section 3).