Available online at www.sciencedirect.com

ScienceDirect

Geochimica et Cosmochimica Acta 71 (2007) 5500–5513

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Olivine/melt transition metal partitioning, melt composition, and melt structure—Influence of Al^{3+} for Si^{4+} substitution in the tetrahedral network of silicate melts

Bjorn O. Mysen

Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road, NW, Washington, DC 20015, USA

Received 26 February 2007; accepted in revised form 20 September 2007; available onilne 29 September 2007

Abstract

The influence on olivine/melt transition metal (Mn, Co, Ni) partitioning of $Al^{3+} \Longleftrightarrow Si^{4+}$ substitution in the tetrahedral network of silicate melt structure has been examined at ambient pressure in the 1450–1550 °C temperature range. Experiments were conducted in the systems $NaAlSiO_4$–Mg_2SiO_4– SiO_2 and $CaAl_2Si_2O_8$–Mg_2SiO_4–SiO_2 with about 1 wt% each of MnO, CoO, and NiO added. These compositions were used to evaluate how, in silicate melts, $Al^{3+} \Longleftrightarrow Si^{4+}$ substitution and ionization potential of charge-balancing cations affect activity–composition relations in silicate melts and mineral/melt partitioning.

The exchange equilibrium coefficient, $K_{D(\mathrm{M-Mg})}^{\mathrm{olivine/melt}} = (X_{\mathrm{M}}/X_{\mathrm{Mg}})^{\mathrm{olivine}}/(X_{\mathrm{M}}/X_{\mathrm{Mg}})^{\mathrm{melt}}$ ($\mathrm{M} = \mathrm{Mn}^{2+}, \mathrm{Co}^{2+}, \mathrm{Ni}^{2+}$), is a positive and linear function of melt Al/(Al + Si) at constant degree of melt polymerization, NBO/*T*. The $\partial[K_{D(\mathrm{M-Mg})}^{\mathrm{olivine/melt}}]/\partial[\mathrm{Al}/(\mathrm{Al}+\mathrm{Si})]$ is negatively correlated with the ionic radius, *r*, of the M-cation and also with the ionization potential (Z/r^2, Z = electrical charge) of the cation that serves to charge-balance Al^{3+} in tetrahedral coordination in the melts.The activity coefficient ratio, $(\gamma_{\mathrm{M}}/\gamma_{\mathrm{Mg}})^{\mathrm{melt}}$, is therefore similarly correlated.

These melt composition $K_{D(\mathrm{M-Mg})}^{\mathrm{olivine/melt}}$ relationships are governed by the distribution of Al^{3+} among coexisting Q-species in the peralkaline (depolymerized) melts coexisting with olivine. This distribution controls Q-speciation abundance, which, in turn, controls $(\gamma_{\mathrm{M}}/\gamma_{\mathrm{Mg}})^{\mathrm{melt}}$ and $K_{D(\mathrm{M-Mg})}^{\mathrm{olivine/melt}}$. The relations between melt structure and olivine/melt partitioning behavior lead to the suggestion that in natural magmatic systems mineral/melt partition coefficients are more dependent on melt composition and, therefore, melt structure the more alkali-rich and the more felsic the melt. Moreover, mineral/melt partition coefficients are more sensitive to melt composition the more highly charged or the smaller the ionic radius of the cation of interest.

1. INTRODUCTION

Existing data on element partitioning between minerals and silicate melts suggest considerable influence of melt composition (e. g., Watson, 1977; Hart and Davis, 1978; Mysen and Virgo, 1980; Libourel, 1999; Kushiro and Mysen, 2002; Toplis, 2005; Schmidt et al., 2006). In order to understand how melt composition can be related to mineral/melt partitioning it is necessary to develop a quantitative understanding of how composition governs structure and how, in turn, melt structure can be related to activity–composition relationships and mineral/melt partition coefficients. Attainment of such understanding is best accomplished by probing the structure and element partitioning in chemically simple systems where the influence individual variables (composition, temperature, pressure, or other intensive variables) can be varied one at a time. Determination of partitioning behavior in complex silicate systems, using empirical or semi-empirical correlations with melt and mineral compositions (e.g., Hart and Davis, 1978; Colson et al., 1988; O'Neill and Eggins, 2002; Toplis, 2005) may provide useful parameterization of relationships of partition coefficients with melt composition. However,

---

E-mail address: bmysen@ciw.edu

0016-7037/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.gca.2007.09.021

because of the empirical nature of this approach, great caution should be exercised in application of reported relationships with melt composition outside the range within which the experimental calibration was carried out because we cannot determine whether effects cancel out and whether individual effects of composition are correlated. Moreover, as is well established in crystal chemistry, structure governs solubility and solution mechanisms of the components (e.g., Goldschmidt, 1926; Smyth and Bish, 1988; Blundy and Wood, 1994). It follows, therefore, that melt structure governs solubility and solution behavior in melts. Empirical correlations with oxide components offer little insight into structure/solution behavior and have little predictive power. Here, we will, therefore, examine how melt structural information can be used to characterize activity–solution behavior in melts and the implication of such behavior for mineral/melt partition coefficients.

The structural variables most likely responsible for effects of melt composition on partitioning behavior are degree of polymerization, NBO/*T*, proportion and types of Q-species, metal-oxygen bond strength, $Al^{3+} \Longleftrightarrow Si^{4+}$ substitution, and nature of the charge-balance of Al^{3+} in tetrahedral coordination (see also Mysen and Richet, 2005, in particular Chapters 7, 9, and 17). For example, most major, minor, and trace elements are network-modifiers and form bonds with nonbridging oxygen in the Q-species in silicate melts (Mysen, 2003). It is not surprising, therefore, that the proportion of nonbridging oxygens to tetrahedrally coordinated cations, NBO/*T*, often can be correlated with crystal-liquid partition coefficients (e. g., Mysen and Virgo, 1980; Kohn and Schofield, 1994; Jana and Walker, 1997; Toplis and Corgne, 2002; Kushiro and Mysen, 2002). There is, however, no simple and unifying relationship between NBO/*T* of melts and mineral/melt partition coefficients. This lack of a general relationship together with the often significant data scatter in NBO/*T*-based models point to the need to address the solution behavior (structural role) of network-modifying cations in silicate melt in greater detail than so far has been the case.

Network-modifying cations are bonded to nonbridging oxygen in silicate melts. To assess how activity–composition relationships of such cations are related to types and proportions of nonbridging oxygen, it is recalled that silicate melt structure can be described in terms of a small number of coexisting Q-species (e.g., Virgo et al., 1980; Schramm et al., 1984; Stebbins, 1987). These Q-species are defined in terms of their different number of bridging oxygen. They are linked together via the nonbridging oxygens. Each of the nonbridging oxygens in a tetrahedron of a given Q-species is bonded to a tetrahedrally coordinated cation (typically Al^{3+} and Si^{4+}) and a network-modifying cation (typically alkali metals and alkaline earths).

The strength of bonding between network-modifying cations and nonbridging oxygens affects numerous melt properties including thermodynamics of mixing. This bond strength depends on both the ionization potential of the network-modifying cation and on the number of nonbridging oxygen in individual Q-species (Maekawa et al., 1991; Kohn and Schofield, 1994; Mysen and Shang, 2005). Type and abundance of Q-species are, therefore, important structural variables that control solution behavior of network-modifying cations in silicate melts.

The main melt composition variables affecting the type and abundance of Q-species in silicate melts are: (i) the ratio of network-modifying cation per tetrahedrally coordinated cations, (ii) the ionization potential of the network-modifying cations, and (iii) the types and proportion of tetrahedrally coordinated cations. In order to understand how these structural variables affect crystal/melt partition coefficients, we need to evaluate how each and every compositional variable *individually* affects melt structure and how that information can be related to the activity–composition relations of metal cations in silicate melts. Point (i) has been addressed in many experimental studies of relationships between partition coefficients and melt polymerization, NBO/*T*, as summarized above. Point (ii) relates to the proportion of individual Q-species and how their type and abundance are governed by the overall degree of melt polymerization, NBO/*T*, and the ionization potential of individual network-modifying cations that form bonding with nonbridging oxygen in the Q-species (e. g, Mysen et al., 1982; Stebbins, 1987; Maekawa et al., 1991; Mysen, 1997; Jones et al., 2001; Lee and Stebbins, 2003). These aspects of Q-speciation behavior affect crystal/liquid partitioning behavior (Mysen and Dubinsky, 2004; Mysen and Shang, 2005; Mysen, 2006, 2007a).

In this report we will focus on types and proportions of tetrahedrally coordinated cations [Point (iii) above]. This is important for several melt structural reasons. For example, in peralkaline aluminosilicate melts, Al^{3+} is distributed between the coexisting Q-species with a distinct preference of Al^{3+} for the most polymerized of available Q-species (Mysen et al., 1981, 2003; Merzbacher et al., 1990; Cormier and Neuville, 2004; Neuville et al., 2006). This preference leads to a positive correlation, at constant temperature, of Al/(Al + Si) and the equilibrium constant for the Q-speciation reaction,

$$2Q^n \rightleftharpoons Q^{n-1} + Q^{n+1}. \tag{1}$$

Quantitatively, the relationship between equilibrium (1) and Al/(Al + Si) depends on the NBO/*T*, types of Q-species, and how Al^{3+} in tetrahedral coordination is charge-balanced (Roy and Navrotsky, 1984; Galakhov et al., 1985; Lee et al., 2003; Allwardt et al., 2003; Mysen et al., 2003; Allwardt and Stebbins, 2004; Mysen, 2007b). Therefore, because Q-species types and abundance govern the solution behavior of network-modifying cations in silicate melts, it follows that variations in Al/(Al + Si) would also affect this solution behavior and, therefore, mineral/melt partitioning.

This latter observation translates to a need to understand how structural factors resulting from $Al^{3+} \Longleftrightarrow Si^{4+}$ substitution may affect transition metal (Mn, Co, and Ni) partitioning between olivine and melt. This is the objective of the present study. To this end, compositions in the systems $NaAlSiO_4$–Mg_2SiO_4–SiO_2 and $CaAl_2Si_2O_8$–Mg_2SiO_4–SiO_2 have been investigated. These two systems were chosen to assess the effect of Al/Si and different charge-balancing cations of tetrahedrally coordinated Al^{3+} under ambient-pressure, isothermal conditions.