Physical basis of trace element partitioning: A review

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ABSTRACT

Experimental observations on the dissolution of elements in minerals and melts and the partitioning between the two materials show that the concentration (or the partition coefficient) of trace elements depends on the properties of elements as well as those of relevant materials (minerals and melts) and the thermochemical conditions. Previous models of element solubility in minerals contain a vague treatment of the role of the stiffness of the element and have a difficulty in explaining some observations including the solubility of the noble gases. A modified theory of element solubility in minerals is presented where the role of elasticity of both matrix mineral and the element is included using the continuum theory of point defects by Eshelby (1951, 1954, 1956). This theory provides a framework to explain the majority of observations and shows a better fit to the published results on the effective elastic constants relevant to element partitioning. However, the concept of “elasticity of the trace element” needs major modification when the site occupied by a trace element has large excess charge. The experimental data of the solubility coefficients of noble gases in melts show strong dependence on the atomic size that invalidates the “zero-charge” model for noble gas partitioning. A simple model of element solubility in melts is proposed based on the hard sphere model of complex liquids that provides a plausible explanation for the difference in the dissolution behavior between noble gases and other charged elements. Several applications of these models are discussed including the nature of noble gas behavior in the deep/early Earth and the water distribution in the lithosphere/asthenosphere system.

Keywords: Element partitioning, point defects, the Onuma diagram, strain energy model, hard sphere model, noble gas, Invited Centennial article, Review article

INTRODUCTION

The distribution of elements in various materials on Earth has been used to infer the chemical evolution of Earth including the history of partial melting and degassing that has created the crust, atmosphere, and oceans (e.g., Allègre 1982; Allègre et al. 1987; Hofmann 1997; Matsui et al. 1977). The distribution of elements is controlled largely by the difference in the excess free energy of a given element in co-existing materials (e.g., Blundy and Wood 2003; Matsui et al. 1977; Nagasawa 1966), although kinetic factors might also contribute if diffusion is slow (e.g., Lee et al. 2007; Van Orman et al. 2002). When we assume chemical equilibrium to simplify the discussion, then the element distribution is controlled by differences in the excess free energy of elements in coexisting materials such as minerals and melts.

The concentration of trace elements in minerals and melts changes with the physical and chemical conditions as well as the properties of minerals (melts) and elements. Consequently, understanding the controlling factors of concentration of elements in minerals and melts will help us understand the physical and chemical processes in Earth. This is an area where mineralogists (mineral physicists) can make an important contribution to geochemistry.

Obviously, the most direct and crucial studies would be the experimental studies on element partitioning, but experimental studies of partitioning (solubility1) are challenging and the data set is incomplete particularly under the deep Earth conditions. In some cases, there are large discrepancies among published results [e.g., a case of noble gas partition coefficients in olivine and clinopyroxene: (Broadhurst et al. 1992; Hiyagon and Ozima 1986)]. In the case of Ar, for example, even the issue of whether Ar behaves like a compatible or an incompatible element upon partial melting (or solidification from the melt) is controversial (e.g., Broadhurst et al. 1992; Shcheka and Keppler 2012; Watson et al. 2007). Understanding the theoretical basis for dissolution of elements will help assess the experimental observations.

In most of geochemical studies, we focus on the partitioning of trace elements (elements with small concentration) because they are believed to behave as a passive marker of physical/chemical processes (such as partial melting) without changing the nature of the processes themselves. In these cases, the essence of the theory of solubility of trace elements in minerals is much the same as the theory of point defects in solids: both point defects and trace elements are “impurities” in nearly

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1 I use the term “solubility” in a broad sense, meaning the amount of an element in a material in the given thermo-chemical environment.