Theory of elemental fractionation on growing crystal surface

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Some minerals exhibit spatial inhomogeneity in chemical compositions (zoning profile). It is often observed in the composition of solid solutions such as olivine and plagioclase, and in the distribution of the content of trace elements contained as impurities such as titanium in quartz. The zoning profile provides a clue to the environment in which the mineral was formed. The zoning profile is thought to reflect the compositional changes of the surrounding environment (magma or solution, hereafter referred to as "liquid phase") associated with mineral growth. A factor that influences the zoning profile is an elemental diffusion in the liquid phase [1]. If the mineral growth is slow enough, the composition in the liquid phase is homogenized by diffusion and the zoning profile is simply a function of solidification fraction. However, if the mineral growth is fast, the diffusional homogenization cannot keep up with the compositional change in the liquid phase, and a concentration gradient is generated around the growing mineral (boundary layer). In such cases, the zoning profile becomes depending on the crystal growth rate [2]. While the occurrence of the boundary layer complicates the formation process of the zoning profile, it also provides a clue to infer the timescale of the mineral growth. Therefore, the effect of the boundary layer on the zoning profile has been modeled and theoretically investigated [3]. Most of these conventional models assumed a local chemical equilibrium at the solid-liquid interface. Some models assume that the partition coefficient at the interface varies with the crystal growth rate [4], but the assumed dependence was a convenience to reproduce the observed results. Depending on how one assumes the uptake of elements at the interface, the interpretation of the formation of minerals can vary significantly [1]. Therefore, it is important to model how the elemental fractionation on the growing solid-liquid interface depends on what factors with respect to the formation of the zoning profile.

I recently proposed a theoretical model of elemental fractionation based on the classical theory of crystal growth, that takes into account the surface processes of elements. On a faceted surface of minerals, there are steps with a height of one molecule as shown in figure. The growth units such as solute molecules are successively incorporated into the crystal lattice at the step edges, resulting in the step moving forward and the surface building up layer by layer. This growth mechanism is called "layer-by-layer growth," and the crystal growth theory based on it is called the Burton-Cabrera-Frank (BCF) theory [5]. The BCF theory is widely cited as a model that appropriately describes the dependence of the growth rate on supersaturation (or supercooling) not only for crystals made of inorganic materials such as minerals, but also for crystals made of organic molecules such as proteins and amino acids. The original BCF theory dealt only with the molecules that mainly make up the crystal (host molecules), but if impurities were present in the liquid phase, they would be incorporated into the crystal through the similar process. As a natural extension of the BCF theory, I considered the surface processes of impurity molecules and formulated the fraction of impurity incorporation (partition coefficient) into the crystal as a function of supersaturation [6]. The results showed that when the properties (e.g., surface diffusion coefficient) of the host and impurity molecules on the surface differs, the partition coefficient changes as a function of supersaturation. This suggests that even in situations where no boundary layer develops, the zoning profile changes with the change in the crystal growth rate.

In this talk, I will present an overview of the BCF theory [5] and a theoretical model of the elemental fractionation on the growing crystal surface [6]. I hope to provide a new viewpoint on the formation of the

zoning profile of minerals.

References: [1] M. J. Kohn and S. C. Penniston-Dorland (2017), Rev. Miner. Geochem. 83, 103. [2] V. G. Smith et al. (1955), Can. J. Phys. 33, 723. [3] E. B. Watson and T. Müller (2009), Chem. Geo. 267, 111. [4] T. Shea et al. (2019), Cont. Miner. Petrol. 174, 85. [5] W. K. Burton et al. (1951), Philos. Trans. R. Soc. London Ser.A 243, 299. [6] H. Miura (2020), J. Cryst. Growth 549, 125867.

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