An experimental study of trace-element partitioning between Ti-Al-clinopyroxene and melt: Equilibrium and kinetic effects including sector zoning

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ABSTRACT

Equilibrium and dynamic crystallization experiments were used to determine distribution coefficients (D-values) for the REE and the trace elements Sc, V, Rb, Sr, Y, Zr, Nb, Ba, Hf, Th, and U between Ti-Al-clinopyroxene and melt. Equilibrium values for D correlate well with previous studies where values have been determined. The D-values were also studied as a function of cooling rate. Increased cooling rates produce higher growth rates. At growth rates that exceed the diffusion rates in the crystals, the D-values increase to near unity and the HREE D-values exceed unity only at the most rapid crystal growth rates. The increase in D-values is the result of the inclusion of components into the growing pyroxene from the boundary layer that develops at the crystal-melt interface because of the disparity between the growth and diffusion rates. The origin of sector zoning is best explained as an interplay of primarily crystallographic control with kinetic effects.

Keywords: Partitioning of trace elements, clinopyroxene-melt, equilibrium experiments, rare earth elements, dynamic crystallization experiments, distribution coefficients

INTRODUCTION

An important factor in the evolution of an igneous melt is the partitioning of elements between the melt and the crystallizing minerals. To understand the partitioning of elements between minerals and melt, the concept of a distribution coefficient has been developed. The distribution coefficient (D) is defined as the concentration of an element in a mineral divided by the concentration of that element in the melt (Jones 1995). As part of a general effort to determine distribution coefficients (D-values) for planetary materials (Kennedy et al. 1993, 1994), we have determined the D-values for the rare earth elements (REE), Sc, V, Rb, Sr, Y, Zr, Nb, Ba, Hf, Th, and U between Ti-Al-rich clinopyroxene and melt. Pyroxene is often complexly zoned with both normal and sector zoning. Previous attempts to determine D-values for Ti-Al-rich clinopyroxene show that elements such as Ce vary by a factor of 10 with increasing Fe/(Fe + Mg) (Crozaz and McKay 1990). McKay et al. (1994) recognized sector zoning as a potential problem. They noted that D-values increase with increasing Al and Ti and are thus higher in the sector enriched in these elements. These results suggest that both equilibrium and kinetic effects control partitioning.

We carried out an equilibrium experiment and a series of dynamic crystallization experiments at cooling rates in the range 5–1000 °C/h to explore the effects of kinetics on D-values. The material used for this study is the same as that used by Lofgren and Lanier (1992) to study the equilibrium and dynamic crystallization properties of the Angra dos Reis meteorite. This bulk composition is unusual in that it crystallizes Ti-Al-rich clinopyroxene on the liquidus at 1263 °C at 1 atm pressure, and clinopyroxene is the only phase to crystallize for almost 200 °C. The next phase to crystallize is rhonite at approximately 1075 °C. This property allows us to study the crystallization of pyroxene over a large temperature interval without the presence of another phase. We were able to crystallize a large fraction of the liquid as pyroxene alone and produce crystals large enough to analyze with an ion microprobe, even at very rapid cooling rates. In each of the charges, we identified the sector zoning in the clinopyroxene and determined the major-element compositions. We then measured the concentrations of trace elements in both the high-Al, Ti and low-Al, Ti sectors. Our experiments confirm the universal presence and importance of sector zoning in these Ti-Al-rich clinopyroxene and the associated chemical variations. The dynamic crystallization experiments confirm the importance of kinetic controls on growth for the partitioning of elements in clinopyroxene. These data provide insight into the kinetics of the crystallization process and the partitioning of minor and trace elements over a wide range of crystallization conditions.

TECHNIQUES

Experimental methods

The starting material used in this study approximates the composition of the Angra dos Reis meteorite (ADOR) as determined by Mittlefehldt and Lindstrom (1990), and was prepared from reagent grade chemicals homogenized by melting (Table 1). The glassy starting material was then doped with trace elements at levels of 2 to 600 ppm. Trace elements were added to the powdered mixture as 3 separate solutions similar to those used by Kennedy et al. (1993, 1994) to achieve the following approximate concentrations: (1) REE = 100× chondrites; (2) Cs and Ba = 50 ppm, Sr = 100 ppm, and U and Th = 300 ppm; and (3) Zr, Nb, and Hf =...