On the origin of size-dependent and size-independent crystal growth: Influence of advection and diffusion

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ABSTRACT

Crystal growth experiments were conducted using potassium alum and calcite crystals in aqueous solution under both non-stirred and stirred conditions to elucidate the mechanism for size-dependent (proportionate) and size-independent (constant) crystal growth. Growth by these two laws can be distinguished from each other because the relative size difference among crystals is maintained during proportionate growth, leading to a constant crystal size variance ($\sigma^2$) for a crystal size distribution (CSD) as the mean size increases. The absolute size difference among crystals is maintained during constant growth, resulting in a decrease in size variance. Results of these experiments show that for centimeter-sized alum crystals, proportionate growth occurs in stirred systems, whereas constant growth occurs in non-stirred systems. Accordingly, the mechanism for proportionate growth is hypothesized to be related to the supply of reactants to the crystal surface by advection, whereas constant growth is related to supply by diffusion. Paradoxically, micrometer-sized calcite crystals showed proportionate growth both in stirred and in non-stirred systems. Such growth presumably results from the effects of convection and Brownian motion, which promote an advective environment and hence proportionate growth for minute crystals in non-stirred systems, thereby indicating the importance of solution velocity relative to crystal size. Calcite crystals grown in gels, where fluid motion was minimized, showed evidence for constant, diffusion-controlled growth. Additional investigations of CSDs of naturally occurring crystals indicate that proportionate growth is by far the most common growth law, thereby suggesting that advection, rather than diffusion, is the dominant process for supplying reactants to crystal surfaces.

INTRODUCTION

An understanding of the mechanisms of crystal growth and resultant crystal size distributions (CSDs) is important because geological information can be deduced from the shapes of CSDs if the relations between these shapes and the underlying geological processes are understood. Although a considerable amount of research has focused on studying crystal growth based on CSDs, results have been inconsistent, leading to contradictory interpretations of crystal growth mechanisms. Attempts to model crystal growth mathematically have fared little better, as they often fail to predict either the commonly observed lognormal size distribution or the associated crystal size variance (Eberl et al. 2002a).

One controversy surrounding earlier studies involves interpretation of crystal growth in terms of size-independent (constant) vs. size-dependent (proportionate) growth (Eberl et al. 2002a). This paper will explore the origins of these two growth mechanisms, how these types of growth affect the CSD shape, and how they can be affected by environmental conditions. These growth mechanisms, investigated with experiments using potassium alum and calcite crystals grown in both unstirred and stirred aqueous solutions, are presumed to have occurred under conditions of supply-controlled growth, when the rate-controlling step is the supply of reactants to the crystal surface, either by diffusion or by advection. This type of growth contrasts with surface-controlled growth, where the supply of reactants exceeds the growth rate.

Three CSD shapes commonly are formed early in the crystallization process: lognormal, asymptotic, and a “universal steady-state” shape consistent with a process of Ostwald ripening (Eberl et al. 1998; Kile et al. 2000). The initial CSD shape then may be modified during subsequent supply-controlled growth that can be described by constant growth, by proportionate growth, or by some combination of the two; usually, it is during this phase of growth when most of the crystal mass is added. Several other growth laws are possible (see below), but have not been detected in our experiments.

GROWTH EQUATIONS

Constant growth was described by McCabe in 1929, who postulated a “$dL$ law”, whereby crystallographically equivalent faces on similar crystals would grow at the same rate. This growth law has been approximated by $dr/dt = k$ (Nordeng and Sibley 1996; Kile et al. 2000), where $r$ is the crystal radius and $k$ is a constant.

Constant (size-independent) growth can be simulated mathematically by:

$$X_{j+1} = X_j + k_j,$$

where $X_j$ is the crystal diameter after $j$ time intervals or steps (or $j$ iterations of the equation), and $k_j$ is a constant that is ap-