Solid-solid reactions mediated by a gas phase: An experimental study of reaction progress and the role of surfaces in the system olivine+iron metal

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Abstract

The intergranular fluid involved in solid-solid reactions is tacitly assumed to be a melt or a (C-O-H-S-Cl-F)-bearing phase. We have studied the system olivine+metal using diffusion couple experiments, in situ reaction progress monitoring using Knudsen-cell mass spectrometry, and thermodynamic-kinetic analysis to show that a dry vapor phase coexisting with solids (silicates, oxides, metals) has all the characteristics of a classical petrologic "intergranular fluid," and it is a viable transport agent for major rock-forming elements such as Mg, Fe, or Si in many petrologic situations. Some of the major conclusions of the work are: (1) ignoring the vapor phase leads to incorrect estimation of degrees of freedom and consequently, incorrect interpretations of mineral assemblages and zonation; (2) normally refractory elements such as Mg may in some cases be more volatile than O_2 ; and (3) reaction modeling using free-energy minimization allows the main parameters controlling reaction progress, pathway, and products (assemblage, abundance of phases, and composition) to be identified. These parameters include: available reactive surface area; volume of the reaction system; diffusion rates in the product solid; temperature; and relative rates of reaction to transport (in/out of the system). Components other than those appearing explicitly in the mass-balance equations (e.g., f_{o_1} in the olivine+metal system) may play an important role. Transport of Mg in the vapor phase away from local reaction sites explains the compositional zoning of olivine around FeNi-metal inclusions and simultaneously provides a mechanism for the growth of at least some of the fayalite-rich rims in Allende and other meteorites of the CV3-class. Similar considerations may play a role in terrestrial problems where metal and silicate coexist, e.g., the primitive terrestrial magma ocean and the "D" layer.