

Element mobility during regional metamorphism in crustal and subduction zone environments with a focus on the rare earth elements (REE)

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ABSTRACT

This paper explores bulk-rock geochemical data for a wide array of metamorphosed mafic, quartzofeldspathic, pelitic, and metacarbonate rocks using a quantitative mass-balance approach to assess fluid-driven element mobility—particularly of the rare earth elements (REE)—in regional metamorphic and some high-pressure subduction zone environments (40 examples; over 240 individual analyses). Most examples are from focused fluid flow settings, such as veins and lithologic contacts, where fluxes are large and metasomatic signals are thus strong. A variety of REE behaviors are observed, including little or no REE mobility (roughly a third of the data set); light REE (LREE), mid-REE (MREE), and/or heavy (HREE) mobility; europium “anomalies”; overall REE losses; and local REE redistribution. The REE are typically fractionated by mass transfer, with the exception of several examples that underwent fairly uniform overall losses of REE. The fractionation reflects strong mineralogical controls on REE uptake/loss by a comparatively small number of phases. Examples include: HREE mass changes associated with garnet, xenotime, and sphene; LREE and MREE changes associated with apatite, monazite, and allanite; and Eu changes associated with plagioclase and lawsonite. As mineralogy is a dominant control, the nature of the metasomatism is not strongly correlated with metamorphic grade, other than obvious mineralogical differences between settings (e.g., plagioclase in Barrovian metamorphism, lawsonite in subduction zones). Extensive mobilization of non-REE major and trace elements can happen without significant open-system transport of the REE. If REE mobility occurs, it is always accompanied by mobilization of other non-REE. When mobile, neighboring REE (e.g., Sm and Nd) typically have strongly correlated mass changes indicating that both were mobilized to about the same degree. Although individual examples of metasomatism can show correlations between patterns of mass transfer for the REE and the non-REE, little such correlation is evident across the entire data set, with the exception of P. Once again, this highlights the importance of individual minerals in controlling REE systematics. Broad correlations of REE and P mobility suggest REE transport by P complexes, or REE and P transport together by some other complexing agent. Mass changes for REE and Y are more strongly coupled, reflecting the geochemical similarity of these elements and perhaps indicating a role for Y complexing as well.

The REE are the most mobile of the high field strength elements (HFSE). On a percentage mass basis, the amount of HFSE mobility decreases roughly in the order: REE > U > Nb > Ti > Th ~ Zr. Th mobility is rare but when present is positively correlated with U and REE mobility. The mobility of the more refractory HFSE is low in aqueous fluids, but is a larger concern in more extreme environments such as magmatic/magmatic-hydrothermal systems, charnockite metamorphism, and supercritical fluids in high-pressure/ultrahigh-pressure settings. The mobility of certain HFSE (e.g., Nb) can be large enough to affect rock plotting positions on petrotectonic discrimination diagrams.

Potassium and related (Rb, Ba, Cs) large-ion lithophile elements (LILE) are typically lost in association with mica breakdown. As the data set focuses on high fluid flow environments, LILE changes will likely be smaller for rocks that undergo less fluid-rock interaction. Gains of K and related LILE are coupled to volatile gain and Na loss, consistent with fluid flow down temperature gradients, or infiltration from K-rich sources (e.g., pegmatites). In Barrovian settings, two other mass transfer trends are evident in addition to K mass transfer. First, silica loss is coupled to volatile loss, illustrating the dependence of silica mass transfer on devolatilization. Most of the silica loss reflects local mass transfer into adjacent vein fluid flow conduits where additional silica is precipitated; indeed, wallrock inclusions in veins can be highly silicified. Second, Na and Ca mass gains and losses are well correlated in the Barrovian examples, reflecting control of plagioclase growth or destruction. Strontium and Pb behaviors also appear to be largely related to plagioclase behavior (in subduction settings, this role can be played by phases such as lawsonite or epidote group minerals).

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Carbon dioxide mass transfer by conventional devolatilization as well as near-stoichiometric CaCO_3 dissolution or precipitation is represented in the data set. Determining the relative roles of these processes as functions of metamorphic grade, intensity of fluid-rock interaction, and tectonic setting will be an important challenge for future research.

Keywords: Rare earth elements, fluid flow, mass transfer, metasomatism, metamorphism, Barrovian metamorphism, subduction zones