Rare earth element mobility at constant inter-REE ratios in the alteration zone at the Phelps Dodge massive sulphide deposit, Matagami, Quebec

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Abstract. Rare earth elements (REE) from La to Ho were mobile and enriched in hydrothermally altered rocks below the Archean Phelps Dodge Cu-Zn volcanogenic massive sulphide deposit in northwestern Quebec. Largest net enrichment was in the moderately altered quartz-chlorite zone where La concentration increased six-fold and La/Yb increased steepened from 1.9 to 13.0; the intensely altered chlorite zone had both minor net REE enrichment and depletion. Yb and Lu were immobile throughout both zones. The mobile REE were added and subtracted in constant chondrite-normalized inter-REE proportions: 1.0 La, 0.79 Ce, 0.57 Nd, 0.49 Sm, 0.01 Eu, 0.10 Tb and 0.02 Hb. Small additions of Eu relative to generally larger additions of LREE and Tb produced enhanced negative Eu-anomalies. The REE were mobilized at the hot (> 300 °C) core of the alteration system and deposited at the cooler periphery. Other sites of intense alteration and water/rock interaction display similar REE changes, indicating that selective REE enrichment at constant inter-REE ratios is a widespread phenomenon.

The rare earth elements (REE) are widely used in geochemical studies, in mineral exploration, and in research on the genesis of ore deposits and their enclosing wallrocks. The REE are particularly helpful in establishing volcanic stratigraphy in greenstone belts owing to their high incompatibility in most igneous processes, their subtle intra-group chemical differences, and their purported low mobility in water/rock interactions (Humphris 1984). However, minor mobility of the REE has been recorded in some studies of low grade metamorphism (Wood et al. 1976, Hellman et al. 1979, Ludden and Thompson 1979, Bartley 1986) and hydrothermal alteration (Kerrich and Fryer 1979, Campbell et al. 1984, Ludden et al. 1984, Bence and Taylor 1985, Lesher et al. 1986), and this could be problematic in some geochemical studies. The REE are particularly useful in distinguishing tholeiitic and calc-alkaline volcanic rock series, and are becoming increasingly important as a direct exploration tool for Archean volcanogenic massive sulphides (MacGeehan and MacLean 1980a, b, Campbell et al. 1984, Lesher et al. 1986). For these reasons any deviations from normal REE geochemical behavior must be recognised.

Altered host rocks at the Phelps Dodge massive sulphide deposit are of interest because of an abnormally high enrichment of the light REE (LREE) in a stratiform chloritized rhyodacite unit directly below the ore. The samples in this study are from a set used by Kranidiotis (1985) and MacLean and Kranidiotis (1987) who demonstrated that Al, Zr, Nb, Ti and Y were immobile during the alteration process. In those studies any two of the above elements plotted against each other for this rock unit exhibited a high correlation coefficient. Furthermore, a best-fit regression line through these data passed through the presumed precursor rock composition and the origin. This latter test is critical; otherwise, the elements may have been mobile in one stage of alteration and immobile in another, or rocks of dissimilar composition inadvertently may have been used (Finlow-Bates and Stumpf 1981; MacLean and Kranidiotis 1987). Using these immobile elements as monitors MacLean and Kranidiotis (1987) calculated gains and losses of other constituents: mass and volume changes were found to range up to 60–70%. With these tight controls on gains and losses of constituents, the study was extended to an examination of changes in the REE during the alteration process.

Phelps Dodge deposit

The deposit is located 40 km west of the Matagami mining district which lies in northwestern Quebec on the northern side of the Archean Abitibi Greenstone Belt (Fig. 1). The geology of the deposit is described by Kanidiotis (1985) and MacLean and Kranidiotis (1987). It is a small (2 million tonnes), steeply dipping, stratiform lens of Cu-Zn massive sulphide ore enclosed in felsic volcanic lavas and volcanioclastic rocks (Fig. 2). Basaltic and basaltic-andesite units occur higher and lower in the mine stratigraphy. These rocks are enriched tholeiites (high concentrations of Fe, Ti, Y, Zr, Nb, REE; low Mg), and have characteristic flat chondritic-normalized REE profiles (Fig. 4a). They are petrographically and chemically very similar to enriched tholeiites at the main Matagami camp (MacGeehan and MacLean 1980a; MacLean 1984). Higher in the stratigraphy are a series of calc-alkaline pillow flows similar to those mapped by Beaudry (1984) on the western side of the Matagami district. Metamorphism in the area attained the middle greenschist facies. The ore lens and an underlying bed of altered volcanioclastic rocks (Fig. 2) lie on the flank of a small felsic dome. The orebody is channel-shaped, finely banded, pyritic, and lacks a typical underlying alteration pipe. It was probably deposited as a sediment at some distance from an exhalative center.
Fig. 1. Location map and position of the Phelps Dodge massive sulphide deposit within the Archean Abitibi Greenstone Belt in the Canadian Shield in northwestern Quebec. 1 - older gneisses, 2 - Abitibi greenstone rocks, 3 - layered gabbroic Bell River Igneous Complex, 4 - granitic rocks

Fig. 2. Geological cross-section through the Phelps Dodge deposit, simplified after Kranidiotis (1985). 1 - glacial overburden, 2 - gabbro, 3 - dacite, 4 - sulphide ore, 5 - chloritite, 6 - rhyodacite and quartz-chlorite rock, 7 - rhyolite

Altered rocks

The rhyodacite unit forming the basis of the present and previous studies consists of altered aphyric lava, breccia, and the bed of fine grained volcanlastic rocks below the ore lens (Fig. 2). The metamorphic assemblage quartz-

albite-epidote-chlorite±sericite in the least altered rhyodacite gives way to the quartz-chlorite±sericite±talc assemblage (quartz-chlorite rock) in parts of the lava and breccia, and to chlorite±sericite±talc assemblage (chloritite) in most of the volcanlastic bed (Kranidiotis and MacLean 1987). Calcite and stilpnomelane are minor constituents in a few of the altered rocks, and leucochrome is sparse but ubiquitous. Pyrite, pyrrhotite, chalcopyrite and sphalerite, which comprise the bulk of the ore lens, are present in minor to trace amounts in the chloritite. Although magnetite is common in the ore, it is absent in the chloritite.

The major chemical changes from least altered rhyodacite (precursor rock composition) to quartz-chlorite rock, outlined in detail by MacLean and Kranidiotis (1987), are the total loss of Na and Ca (except where calcite is present), pervasive additions of Mg and Fe, and local additions of silica. The chloritites have much lower Si, and higher Al, Mg and Fe than the quartz-chlorite rocks, owing to in situ leaching of quartz which reduced both mass and volume of the rock by 60 to 70 percent and concurrently enriched the immobile elements.

Chemical data

Chemical analyses for the REE were made by the instrumental neutron activation method at the GINA Laboratory, University of Montreal. Analytical techniques and precision are discussed in Ludden et al. (1984). Other elements were analysed by X-ray fluorescence at the Department of Geological Sciences, McGill University. The analyses data of these elements, may be obtained from the author on request. Correlation coefficients for the REE and a selection of other elements are listed in Table 1.

Correlation coefficients

The LREE have very high correlation coefficients with each other but low correlations with other REE (Table 1). Eu does not correlate well with any other REE, and the heavy REE (HREE) correlate well only with each other. The small but steady decreases in values of the coefficients from La to Sm and Lu to Ho probably reflect the gradual lessening of chemical similarity with atomic number separation. The high correlation values among the LREE contrast sharply with the low ones obtained when the LREE are correlated against Al, Zr, Nb, Y and Ti, the established immobile elements in the alteration system with which they have less or no geochemical affinity. The LREE were apparently mobilized, and moved largely as one coherent group. Their low correlation coefficients with the immobile elements do not, by themselves, prove that the LREE were added to or removed from the alteration system; the coefficients may only be a measure of the heterogeneous redistribution of the LREE in the alteration zone. The high correlation coefficients of Lu, Yb and Ho with the immobile elements are, however, evidence the HREE were essentially immobile.

Binary plots

Binary plots of REE using an established immobile element can, as noted earlier, be used as a critical test for gains and losses of material in alteration systems. The Al₂O₃-Zr plot (Fig. 3) illustrates a closely correlated array of data for a immobile pair of elements, with a linear regression line that