

The partitioning of trace elements between ilmenite, ulvöspinel, armalcolite and silicate melts with implications for the early differentiation of the moon

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Abstract

Mineral/melt trace element partition coefficients for a large number of trace elements (Zr, Hf, Ta, Nb, V, Co, Cu, Zn, Sr, REE, Sb, Sn, Mo, Cr, W, U, Th) were determined experimentally for ilmenite (FeTiO₃), ulvöspinel (Fe₂TiO₄), minerals of the armalcolite solid solution (Fe,Mg)Ti₂O₅. The measured partition coefficients indicate that the high field strength elements (Zr, Hf, Nb, and Ta) and some transition metals (V, Cr, Co, Sn) are moderately compatible in iron–titanium oxides, whereas other elements (REE, Y, Sr, U, Th, Mo, Sb, and W) are strongly incompatible. The partition coefficients for U are always significantly higher than the Th partition coefficients which makes Fe–Ti oxides efficient in fractionating U from Th. Our data also indicate that ilmenite, and other iron–titanium oxides, are able to fractionate W from Hf, the latter of which is much more compatible. This makes the iron–titanium oxides very effective agents to influence Hf–W isotopic ratios during the evolution of the moon. In addition, we also present some trace element partition coefficients for iron and titanium-bearing orthopyroxene.

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1. Introduction

Oxides of iron and titanium are ubiquitous accessory phases in igneous, metamorphic, and sedimentary rocks (Haggerty, 1973a; Contini et al., 1993; Hayob and

Essene, 1995; Mitra and Ahmed, 1995; Sengupta et al., 1999; Bingen et al., 2001; Anand et al., 2003; Goodrich, 2003; Mücke, 2003; Topuz et al., 2004; Anderson and Morrison, 2005). The most important iron–titanium oxides, or Fe–Ti oxides, on Earth are ilmenite and titanomagnetite, whereas minerals of the armalcolite solid solution (Mg,Fe)Ti₂O₅ are common on the Moon (Haggerty, 1973a) and rare on Earth (Contini et al., 1993; Hayob and Essene, 1995). Most terrestrial Fe–Ti oxides form part of three complex solid solutions along

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the joins between ilmenite (FeTiO_3) and magnetite (Fe_3O_4), ulvöspinel (Fe_2TiO_4) and hematite (Fe_2O_3), and ferropseudobrookite (FeTi_2O_5) and pseudobrookite (Fe_2TiO_5). The complexity and large chemical and structural variations are mainly due to changes in oxygen fugacity and resulting variations in ferric to ferrous iron ratios. Consequently, on the Moon, with its extremely low oxygen fugacity, common Fe–Ti oxides are ilmenites and minerals of the armalcolite solid solution possessing only divalent iron (Haggerty, 1973a, b). In terrestrial basaltic rocks, the main Fe–Ti oxides are titanomagnetites, whereas ilmenites are much more common in kimberlitic or lamproitic magma (Frost and Lindsley, 1991). In this context, it should also be mentioned that ilmenites are rock-forming minerals in rare mica–amphibole–rutile–ilmenite–diopside (MARID) xenoliths which are probably of metasomatic origin (Dawson and Smith, 1977; Kramers et al., 1983; Sweeney et al., 1993; Wagner et al., 1996; Konzett et al., 1998). Moreover, Cr-bearing ilmenite is also commonly employed as an indicator mineral in diamond exploration (Griffin and Ryan, 1995).

Because of the common occurrence of Fe–Ti oxides in a large number of rocks, a number of previous studies investigated phase relations of Fe–Ti oxides as a function of pressure, temperature, and oxygen fugacity ($f\text{O}_2$) (Buddington and Lindsley, 1964; Readman et al., 1967; Readman, 1978; O'Neill et al., 1988; Frost and Lindsley, 1992; Toplis and Carroll, 1995; Inoue et al., 1996; Ghiorso, 1997; O'Neill, 1998; Feenstra and Engi, 1998; Pownceby and Fisher-White, 1999; Zhao et al., 1999; Lattard et al., 2005). In particular the response of Fe–Ti oxide phase relations to changes in $f\text{O}_2$ has attracted considerable interest as this enables oxygen geobarometry in a wide range of metamorphic and magmatic rocks (e.g., Buddington and Lindsley, 1964; Ghiorso and Sack, 1991; Sack and Ghiorso, 1991; Zhao et al., 1999; Harlov, 2000; Ishihara, 2004).

Despite these previous efforts, however, there is scant data on the geochemical behaviour of Fe–Ti oxides in magmatic systems (Nakamura et al., 1986; Green and Pearson, 1987; Piccoli et al., 2000). This is surprising, as iron–titanium oxides are known to incorporate relatively high concentrations of the high field strength elements (HFSE: Zr, Hf, Nb, Ta) and may, therefore, play an important role in the geochemical cycles of these otherwise incompatible elements. This may be of special importance in subduction zones, as ilmenites and Fe–Ti bearing spinels are important accessory phases in subducting lithosphere. Especially amphibolites, which commonly contain ilmenite as accessory phases, have been identified as a possible

source in the generation of the continental crust (Rapp and Watson, 1995; Foley et al., 2002; Rapp et al., 2003) in a subduction zone environment. Furthermore, not much is known about the potential of iron–titanium oxides to fractionate other geochemically relevant elements such as U, Th, or W. Knowledge of the latter is a prerequisite for our understanding of lunar petrogenesis, as ilmenite is believed to play a major role in fractionating W from Hf (Lee et al., 1997; Righter and Shearer, 2003; Shearer and Righter, 2003; Jacobsen, 2005). However, there is only very little experimental data as to how W partitions between ilmenite and silicate melts (Candela and Bouton, 1990).

In order to further our understanding of the geochemical behaviour of iron–titanium oxides in magmatic systems, we set out to investigate the partitioning of trace elements between different Fe–Ti oxides and silicate melts. Previous experimental work on trace element partitioning is limited to a relatively small number of trace elements (McCallum and Charette, 1978; McKay et al., 1986; Nakamura et al., 1986; Green and Pearson, 1987; Candela and Bouton, 1990; Nielsen et al., 1992). None of the aforementioned experimental studies present a comprehensive set of partition coefficients for all HFSE, which was one of the aims of the present study. Moreover, we also set out to study the partitioning of elements such as Th, U, and W, the latter of which is of great relevance for the interpretation of tungsten isotopic signatures on the Earth, Moon and on Mars (Lee and Halliday, 1997; Shearer and Newsom, 2000; Lee et al., 2002; Schoenberg et al., 2002; Righter and Shearer, 2003; Shearer and Righter, 2003; Kleine et al., 2004).

It should be noted that several previous studies provide constraints on partitioning of a limited number of elements between mineral phenocrysts and a matrix in natural systems (Mahood and Hildreth, 1983; Fujimaki et al., 1984; Nash and Crecraft, 1985; LaTourrette et al., 1991; Ewart and Griffin, 1994; Stimac and Hickmott, 1994). However, these studies are, in principle, much more difficult to interpret when compared to experimentally derived partition coefficients owing to the heterogeneity of natural rock matrices and, thus, the poorly constrained bulk compositions when compared to experimental run product matrices. Furthermore, equilibration between crystals and melts in natural phenocryst/matrix systems is difficult to ascertain. Moreover, as phenocryst/matrix partition coefficients are determined in natural compositions with often very low concentration of the trace element of interest, analyses of phenocrysts are often very close to the analytical detection limit and are,

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