Available online at www.sciencedirect.com

ScienceDirect

Geochimica et Cosmochimica Acta 132 (2014) 170–186

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

An experimental study of trace element partitioning between augite and Fe-rich basalts

Nick Dygert *, Yan Liang, Chenguang Sun, Paul Hess

Department of Geological Sciences, Brown University, Providence, RI 02912, USA

Received 15 July 2013; accepted in revised form 30 January 2014; available online 19 February 2014

Abstract

Aluminous titanium-rich hedenbergite and Fe-rich augite were experimentally produced at 1050–1220 °C and 0.8–2.2 GPa. Major element compositions are analogous to clinopyroxene from layered intrusions, angrites, nakhlites, and late-stage lunar magma ocean cumulates. Trace element concentrations in pyroxene and coexisting melt were measured by laser ablation inductively coupled plasma mass spectrometry for rare earth elements (REE), high field strength elements (HFSE), transition metals, and large-ion lithophile elements. REE, HFSE, and transition metal partition coefficients (*D*s) are tightly correlated with the cation abundance of Fe on the pyroxene M1 site (X_{Fe}^{M1}), and also correlated with Al on the tetrahedral site (X_{Al}^{T}). Parameterized lattice-strain models were developed to predict REE and HFSE partition coefficients as functions of temperature and pyroxene composition (X_{Al}^{T} or X_{Fe}^{M1}). The parameterized models can be used to calculate REE and HFSE partition coefficients for Fe-rich high-Ca pyroxene. We calculated partition coefficients for clinopyroxene derived from modeled end-stage lunar magma ocean cumulate compositions and observe a factor of 3 variation in clinopyroxene-melt REE partition coefficients. Using representative nakhlite clinopyroxene core and rim compositions we calculated partition coefficients and observed a factor of 4 variability in clinopyroxene-melt REE partition coefficients. HFSE partition coefficients are even more sensitive to composition, showing variations of a factor of 4 for lunar late cumulates and an order of magnitude for nakhlites. The strong dependence of REE and HFSE partitioning on composition necessitates careful selection of appropriate partition coefficients for Fe-rich systems.

1. INTRODUCTION

Mineral-melt trace element partition coefficients (*D*s) are important parameters in the interpretation of igneous rocks. Significant progress has been made in characterizing and understanding trace element partitioning between major rock-forming minerals such as pyroxene and basaltic melts (e.g., Wood and Blundy, 2003; Sun and Liang, 2013a, and references therein), although most of the studies published to date focus on mafic and ultramafic systems relevant to the Earth's upper mantle. Recent research focused on developing a robust theoretical framework to predict partition coefficients (e.g., Blundy and Wood, 1994; Sun and Liang, 2013a) and applying it to natural systems, while earlier studies focused on understanding fundamental compositional controls of trace element partitioning. Nakamura et al. (1982) noted a correlation between clinopyroxene Fe/(Fe + Mg) ratio and rare earth element (REE) partition coefficients available at that time, generating an Fe-based partitioning model to predict partition coefficients for nakhlites. McKay et al. (1986) argued that REE partitioning in pyroxene is primarily controlled by its wollastonite content and that partitioning is insensitive to the Fe/Mg ratio of the system. Gallahan and Nielsen (1992) obtained consistent results, proposing that the primary crystal-chemical control

* Corresponding author. Address: 324 Brook Street, Box 1846, Providence, RI 02912, USA. Tel.: +1 617 699 9039.
E-mail address: nicholas_dygert@brown.edu (N. Dygert).

http://dx.doi.org/10.1016/j.gca.2014.01.042
0016-7037/

on partitioning is Ca but that partitioning is also sensitive to the Al content of coexisting melt. Later experimental studies (e.g., Gaetani and Grove, 1995; Lundstrom et al., 1998; Hill et al., 2000) convincingly demonstrated the dependence of REE and high field strength element (HFSE) partitioning on the abundance of tetrahedral Al (X^{T}_{Al}) in magnesian clinopyroxene. Most recently, Sun and Liang (2012) found the cation fractions of Mg on the pyroxene M2 site (X^{M2}_{Mg}) and Al on the tetrahedral (X^{T}_{Al}) and M1 (X^{M1}_{Al}) sites and temperature are the primary factors controlling REE partitioning in clinopyroxene.

Considerably fewer mineral-melt trace element partitioning studies have been done on more Fe-rich systems which are also important to magmatic differentiation in the Earth and planetary bodies. The present study focuses on trace element partitioning between augite and nominally anhydrous Fe-rich basalts, quantifying the relationship between REE and HFSE partition coefficients in Fe-rich augite as a function of composition and temperature. While pure hedenbergite ($CaFeSi_2O_6$) and Fe-rich augite are relatively rare, they crystallize at end-stage solidification of magma oceans and layered intrusions, and from evolved igneous melts on bodies throughout the solar system. Examples of Fe-rich pyroxene in natural rocks are presented in Fig. 1 and include layered intrusions such as the Skaergaard and the Bushveld Complexes (blue and red lines, Fig. 1a, Wager and Brown, 1967), selected ferroan calc-alkaline systems (e.g., white diamonds, Fig. 1b, Olin and Wolff, 2010), angrites (salmon field, Fig. 1a, Kuehner et al., 2006), the Martian nakhlites (yellow and green fields, Fig. 1a, see figure caption for references), lunar alkali suite rocks (pink diamonds, Fig. 1a, Shervais and McGee, 1999), and MAGFOX calculated lunar magma ocean cumulates (green dots, Fig. 1a) (MAGFOX is an experimentally calibrated lunar magma ocean crystallization model developed by Dr. John Longhi (1991)).

Studies investigating trace element partition coefficients between clinopyroxene and basaltic melt for Fe-rich systems are rather limited. Two recent experimental studies investigated clinopyroxene-melt partitioning at intermediate Mg#s [=100 × MgO/(MgO + FeO), in moles], but both use somewhat exotic bulk compositions. Wood and Triglia (2001) report partition coefficients for aluminous clinopyroxene (up to 12 wt% Al_2O_3) with Mg#s of 54–69 in hydrous alkali-rich melts (up to 3 wt% initial H_2O). Their REE partitioning data are included in the study of Sun and Liang (2012) who developed a parameterized lattice strain model for clinopyroxene-melt REE partitioning (see below). Pertermann and Hirschmann (2002) measured clinopyroxene-melt partition coefficients in anhydrous experiments with bulk compositions representing partial melts of a quartz-bearing eclogite ($SiO_2 \sim 57$ wt%). Pyroxenes in their study have Mg#s of 57–60 and exceptionally high Al_2O_3 abundances (up to 17 wt%). Partitioning behavior in these systems is very different than in anhydrous ferro-basalts and we were unable to develop a generalized model to predict partition coefficients of Wood and Triglia (2001), Pertermann and Hirschmann (2002), and our experimental results (see Section 4.1). These studies will not be discussed further.

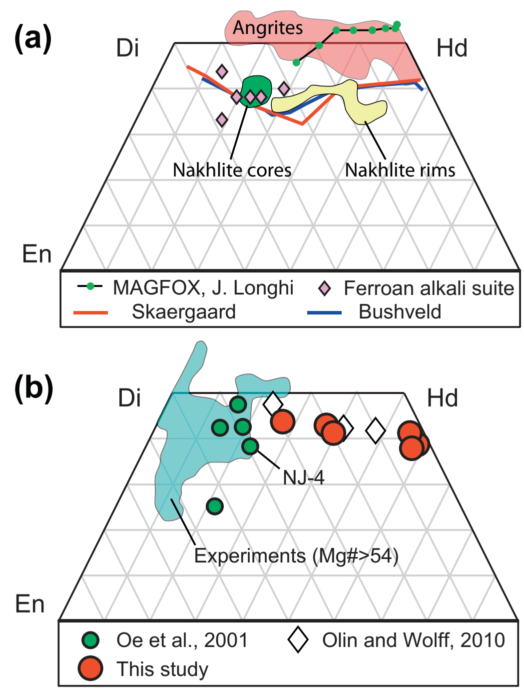

Fig. 1. Examples of naturally occurring Fe-rich pyroxene (a), and pyroxene compositions in selected trace element partitioning studies (b). Fe-rich pyroxene is observed in nakhlite meteorites from Mars (yellow and green fields), the angrite parent body (salmon field), terrestrial layered intrusions (red and blue lines), the lunar alkali suite (pink diamonds), and MAGFOX calculated lunar magma ocean cumulates (green circles joined by black line). Blue field in (b) denotes pyroxene compositions in laboratory trace element partitioning studies that were included in the parameterized lattice strain model of Sun and Liang (2012). White diamonds are clinopyroxene from natural rocks (tuff and phonolite), green circles are nakhlite analogue experiments, and large red circles are from this study. Data used to define nakhlite fields is from Wadhwa and Crozaz (1995), Wadhwa et al. (2004), Day et al. (2006), and Udry et al. (2012). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Very few additional experimental studies exist for trace element partitioning in Fe-rich basaltic systems. Oe et al. (2001) report REE partition coefficients for nakhlite analogue experiments with intermediate Mg#s (green circles in Fig. 1b, green line in Fig. 2a) and noted a correlation between REE partition coefficients and Al_2O_3 in pyroxene. These partition coefficients were calculated from electron microprobe analyses of heavily doped experiments conducted at atmospheric pressure. Because the pyroxene compositions in Oe et al. (2001) closely match those of nakhlite cores (Fig. 1), the partition coefficients were extensively used in petrogenetic modeling of the nakhlites (e.g., Wadhwa et al., 2004; Day et al., 2006; Udry et al., 2012). The number of elements reported in Oe et al. (2001) is limited, however interpolation between middle and heavy REE shows a flat pattern (green line in Fig. 2a). Major element compositions for the study of Oe et al. (2001) were not reported.