Available online at www.sciencedirect.com

ScienceDirect

Chemical Geology 248 (2008) 119–139

CHEMICAL GEOLOGY
INCLUDING
ISOTOPE GEOSCIENCE

www.elsevier.com/locate/chemgeo

Siderophile elements in silicate melts — A review of the mechanically assisted equilibration technique and the nanonugget issue

Werner Ertel [a,*], Donald B. Dingwell [a], Paul J. Sylvester [b]

[a] Earth and Environmental Sciences, LMU — University of Munich, Theresienstrasse 41, 80333 Munich, Germany
[b] Department of Earth Sciences, Memorial University of Newfoundland, 300 Prince Philip Drive, St. John's, Newfoundland, Nfld, Canada A1B 3X5

Received 23 February 2007; received in revised form 17 December 2007; accepted 21 December 2007

Abstract

Solubilities for a wide range of siderophile elements (SE: Ni, W, Re, Ir, Os, Pt, Rh) have been determined in a haplobasaltic melt composition ($An_{42}Di_{58}$) using the mechanically assisted equilibration (MAE) technique. Here we present a review of the data obtained and the experience gained over the past decade using this approach. In particular, the major experimental and analytical challenges encountered (and inferred to result from so-called “nanonugget” formation) are described. After a general background overview of siderophile element solubility experiments, the experimental (MAE) and analytical techniques are described. Major element composition was routinely determined by electron microprobe analyses (EMP), whereas trace elements were determined using a wide variety of analytical techniques (Ni, W: INAA, EMP, ICP-AES; Re, Ir, Pt, Rh and Os: INAA, SIMS, *diss*olution-(diss-ICPMS) and *L*aser *A*blation *I*nductively *C*oupled *P*lasma *M*ass *S*pectrometry (LA-ICPMS)). The last technique, in particular, has demonstrated its powerful capabilities for micro-analyses, supplying information on both absolute trace element concentrations and on small scale heterogeneities in run products.

All investigated SEs exhibit solubilities whose systematic variation with oxygen fugacity (fO_2) is consistent with their presence as stoichiometrically dissolved oxide species in the melt phase. There is no indication of zero-valence species dissolved at any fO_2 condition. In the case of highly-SE (HSE: Pt, Rh, Re, Os, Ir), INAA results appear to indicate a decrease of HSE solubility with decreasing fO_2 down to a fO_2 limit which depends on the investigated HSE. Below this limit, bulk HSE concentrations remain either constant with large variations or increase with further fO_2 decrease. Duplicate analyses of samples by LA-ICPMS reveal increasing amounts of so-called nanonuggets with decreasing fO_2, which lead to high HSE concentrations in the glass samples obtained by bulk analytical methods such as INAA. The formation of HSE (and potentially some SE) nanonuggets in low fO_2 samples raises the question of whether nanonuggets are formed either during the quench by precipitation from precursor species dissolved homogeneously in the melts, or are precipitated *in situ* at high temperature due to true thermodynamic oversaturation.

---

* Corresponding author.
E-mail address: ertel-ingrisch@lmu.de (W. Ertel).

doi:10.1016/j.chemgeo.2007.12.013

The combination of the MAE technique with LA-ICPMS micro-analytical methods has enabled us to extend our knowledge of the solubility behaviour of HSE to unprecedentedly low fO_2 values. Clarification of the solubility mechanism for SE as well as the nanonugget issue, however, will undoubtedly require further novel experimental designs.

Keywords: Highly siderophile elements solubilities; Experimental petrology; Mechanically assisted equilibration technology; LA-ICPMS and nanonuggets; Core/mantle segregation; Accretion of terrestrial planets

1. Introduction

Scientific discussions about accretion and core-formation processes in terrestrial planets often center around the so-called “siderophile” elements. All terrestrial planetary bodies contain an Fe-rich metallic core which segregated from molten silicates of presumably chondritic composition early in their geological histories. The strong partitioning of siderophile elements between these two planetary reservoirs makes them sensitive tools for the investigation of accretion and core-formation related processes.

Geochemically, siderophile elements are subdivided into the moderately siderophile elements (MSE) with metal/silicate partition coefficients of $D^{\text{met/sil}} < 10^4$, and the highly siderophile elements with $D^{\text{met/sil}}$ much larger than 10^4. The HSE comprise the six platinum group elements (Ru, Rh, Pd, Os, Ir, and Pt) as well as Au and Re.

As a group, the HSEs display two noteworthy features: 1) they exist in low but measurable amounts in the Earth’s upper mantle (despite extreme $D^{\text{met/sil}}$: e.g.: Pt $> 10^{15}$: Ertel et al., 1999), and 2) they show nearly chondritic elemental ratios as shown in Fig. 1. These features are quite surprising, in light of their vastly differing a) chemical oxide reduction potentials, b) Henry’s Law activity coefficients in Fe-rich metal, c) metal/sulfide–liquid partitioning behaviour, and d) partitioning behaviour between basaltic melt, solid silicates, and oxides. All of these should have modified chondritic element ratios during accretion and subsequent core-forming processes, and led to vanishingly small HSE abundances in the upper mantle. These observations have generated considerable scientific research over the past two decades aimed at solving the apparent paradox of HSE overabundances and chondritic proportions in the Earth.

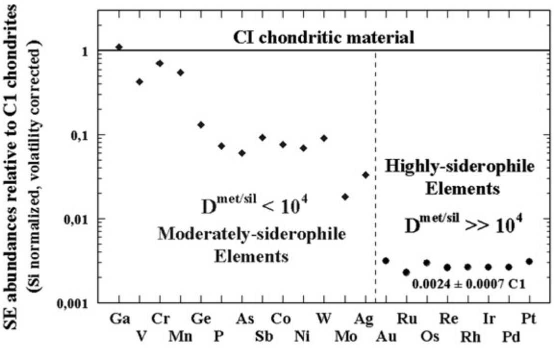

Fig. 1. Abundances of siderophile elements in the Earth’s upper mantle (normalized to CI chondrites and Si) shown with respect to their increasing siderophile affinities (Fe-loving behaviour). Original data from Table 2 of Newsom (1990), McDonough and Sun (1995), and Newsom et al. (1996), reproduced from Ertel-Ingrisch et al. (2006).

Solubility experiments involving highly siderophile elements (HSE) have been attempted for somewhat more than a decade. These efforts have improved our knowledge of their solubility behaviour and pushed back the limits of our experimental techniques and understanding.

First results of experimental investigations about HSE solubilities at 1 atm were presented in the early 1990s. During the following decade, a vast number of solubility studies were performed on: Ir (Amossé et al., 1990; Amossé and Allibert, 1993; Borisov and Palme, 1995a,b; O’Neill et al., 1995; Ertel, 1996; Brenan et al., 2005), Pt (Amossé et al., 1990; Amossé and Allibert, 1993; Azif et al., 1994; Azif et al., 1996; Borisov and Palme, 1997; Ertel et al., 1999; Holzheid et al., 2000; Fortenfant et al., 2003; Brenan et al., 2003; Ertel-Ingrisch et al., 2006), Rh (Capobianco and Drake, 1990; Capobianco et al., 1994; Ertel et al., 1999; Brenan et al., 2003), Au (Capobianco, 1990; Borisov and Palme, 1995b, 1996; Brenan et al., 2005), Pd (Capobianco and Drake, 1990; Capobianco et al., 1991, 1992, 1994; Borisov et al., 1994; Azif et al., 1996; Capobianco and Hervig, 1996; Holzheid et al., 2000; Brenan et al., 2003), Re (O’Neill et al., 1995; Borisov and Palme, 1995a,b; Ertel, 1996; Righter and Drake, 1997; Ertel et al., 2000b, 2001; Brenan et al., 2003), Ru (Capobianco and Drake, 1990; Capobianco et al., 1994; Capobianco and Hervig, 1996; Borisov and Nachtweyh, 1998; Borisov et al., 1999; Brenan et al., 2003), and Os (Borisov and Palme, 1998; Borisov and Walker, 2000; Brenan et al., 2005; Fortenfant et al., 2006). An excellent summary of their results is given in Walter et al. (2000), and summarized in Tables 1 and 2. Most of these investigations were performed between pure metal