Chemical Geology 265 (2009) 512–526

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Accessory phase control on the trace element signature of sediment melts in subduction zones

Jörg Hermann *, Daniela Rubatto

Research School of Earth Sciences, The Australian National University, 0200 Canberra, Australia

ARTICLE INFO

Article history:
Received 7 January 2009
Received in revised form 20 May 2009
Accepted 20 May 2009

Editor: R.L. Rudnick

Keywords:
Subduction recycling
Accessory phases
Large ion lithophile elements
Experimental petrology
Arc magmatism

ABSTRACT

Phase and melting relations in deeply subducted sediments, the main reservoir of large ion lithophile elements (LILE) in subduction zones, are of first order importance to understand the general trace element signature of arc lavas. Here we present results from an experimental study on trace element liberation from metapelites in the range of 2.5–4.5 GPa and 750–1050 °C, i.e., conditions relevant for the slab at sub-arc depth. Apart from the common phases garnet, clinopyroxene, quartz/coesite and phengite, accessory phases such as rutile, apatite, allanite, monazite and zircon occur in the run products.

The hydrous melts produced during wet melting of sediments have been analysed with laser ablation ICP-MS. The minor phase phengite is the main host of LILE in the residue and exerts a strong control on Rb and K in the coexisting melt. The presence of accessory phases profoundly influences the trace element characteristics of the hydrous melts because these phases control several trace elements (Ti by rutile, P by apatite, Zr by zircon, Th and light rare earth elements (Th, LREE) by monazite/allanite). The concentration of these elements in the hydrous melts is primarily a function of temperature and is independent of the amounts of the mineral and melt present. The saturation levels for these elements are used to predict that, in a common subducted sediment, accessory phases are likely to persist up to 850–900 °C at up to 50% melting. Trace element concentrations in hydrous melts are at least one order of magnitude higher than in aqueous fluids. Therefore, sediment melts provide an efficient way of extracting incompatible elements from the subducted slab.

Accessory phases also influence the fractionation of elements with similar geochemical behaviour such as Th/La, Th/U, Ce/Pb (allanite/monazite), Nb/Ta (rutile) and Zr/Hf (zircon). Moreover, phengite is able to retain Rb while Cs is incompatible. These accessory phases therefore control characteristic element fractionation in the subduction component of arc magmas.

1. Introduction

Partial melting is the single most important fractionation process in the differentiation of the silicate Earth. At convergent plate margins new continental crust is formed by “fluid” fluxed mantle melting (Tatsumi and Eggins, 1995). Although we know that this fluid phase[1] is generated in the subducted slab, its nature and composition (aqueous fluid, hydrous melt or transitional, supercritical fluid) is still largely unknown and debated. The composition of subduction-zone fluids can be deduced through geochemistry and petrology.

The geochemical approach of comparing primitive arc lavas to mid ocean ridge basalts (MORB) shows that the slab-derived fluid phase contains significant amounts of volatiles including water and incompatible elements, mainly large ion lithophile elements (LILE), Th, U and some light rare earth elements (LREE) (Hawkesworth et al., 1993; Tatsumi and Eggins, 1995). The correlation between input oceanic crust into subduction zones with incompatible trace element enrichment of arc lavas provides evidence that subducted sediments are the most important hosts of incompatible elements in the slab (Plank and Langmuir, 1993; Plank and Langmuir, 1998). Ratios of elements with different expected mobility in the fluid phase, yet similar compatibilities during partial mantle melting and fractional crystallization are often used to constrain the nature of the slab-derived fluid phase. For example Ba is considered to be highly “fluid mobile” and thus arc lavas showing high Ba/La are interpreted to originate from addition of an aqueous fluid from the slab (Elliott et al., 1997; Pearce et al., 2005). On the other hand, enrichment of “fluid-immobile” Th in arc lavas (high Th/Nb) suggests that sediment melting has occurred (Elliott et al., 1997; Johnson and Plank, 1999). These geochemical studies pay little attention to how

---

* Corresponding author. Mills Road, 0200 Acton, ACT, Australia. Tel.: +61 2 6125 8842; fax: +61 2 6125 8253.
E-mail address: joerg.hermann@anu.edu.au (J. Hermann).

[1] We use the term “fluid” in the most general way as opposed to “solid”. Whenever the nature and composition of such a fluid phase is concerned we specify it either as “aqueous fluid” (water rich, relatively low concentration of solutes), hydrous melt (low water contents, high concentration of solutes) or transitional, supercritical fluid (intermediate between the others).

0009-2541/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemgeo.2009.05.018

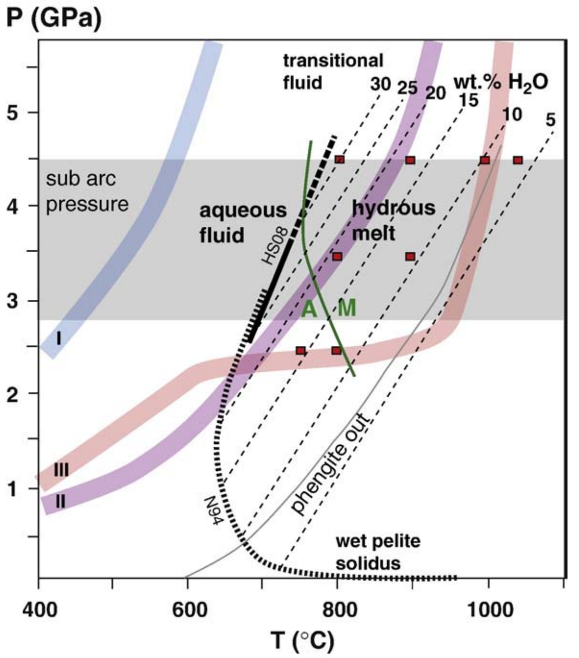

Fig. 1. The position of the wet pelite solidus (dotted line: Nichols et al., 1994; solid line: Hermann and Spandler, 2008) with respect to thermal models for top of slab temperatures (I: Peacock et al., 1994, II: Kincaid and Griffiths, 2004, III: van Keken et al., 2002) determines whether an aqueous fluid, hydrous melt or a transitional fluid is released from subducted sediments at sub-arc depth. Estimated isopleths for the water content of the melt are shown. Squares refer to experiments where trace element concentrations of the hydrous melts have been analysed. Also shown is the stability of phengite, which is the major host for LILE in the solid residue (Hermann and Spandler, 2008). The transition from accessory allanite (A) to monazite (M), which are the main hosts for LREE, Th and U in the residue, is shown.

individual minerals that form in subducted sediments control the distribution and liberation of these elements.

The petrologic approach to constrain the nature and composition of subduction-zone fluids uses phase relations derived from experiments and natural rocks at conditions expected for the slab at sub-arc depths (Poli and Schmidt, 2002; Manning, 2004; Hermann et al., 2006). The depth of the slab below the volcanic arc is typically 70–170 km (Syracuse and Abers, 2006), hence sub-arc pressure ranges from 2.5 to 4.5 GPa. Top of slab temperatures are more difficult to constrain and are largely based on thermal models. The nature and composition of the slab fluid is intimately related to the position of the wet pelite solidus and the top-slab temperature (Fig. 1). For cold slab temperatures (Peacock et al., 1994), models suggest that an aqueous fluid is present. Experimental studies that focused on the liberation of water from the breakdown of hydrous phases in mafic and ultramafic rocks argue for relatively cold top of slab temperatures of 600–700 °C (Ulmer and Trommsdorff, 1995; Schmidt and Poli, 1998). In models that predict intermediate (Kincaid and Griffiths, 2004) and hot (van Keken et al., 2002) slabs, the top of slab temperature is above the wet solidus for pelites (Nichols et al., 1994; Hermann and Spandler, 2008) and sediment melting is expected at sub-arc depth (Fig. 1).

The trace element composition of subduction-zone fluids is conventionally determined through measuring the partitioning between major phases such as garnet, clinopyroxene, and minor rutile with fluids (Brenan et al., 1995; Keppler, 1996; Adam et al., 1997; Ayers et al., 1997; Stalder et al., 1998; Kessel et al., 2005). However, recent studies on subducted crust have shown that these minerals host only a fraction of the incompatible elements and that accessory phases such as allanite and zircon and the minor phase phengite may play a fundamental role in the trace element budget in subduction zones (Hermann, 2002; Spandler et al., 2003). Consequently, the concentrations of several trace elements are possibly controlled by accessory phases and their saturation in subduction-zone fluids (Hermann, 2002; Klimm et al., 2008). If correct, this means that the origin of the subduction component in arc lavas with the characteristic enrichment of LILE, U and to a lesser extent of LREE, Th can only be understood by the study of systems that contain these minerals.

In this paper we link the geochemical and petrological approaches with an experimental study of trace element systematics in hydrous melts produced in subducted sediments, which will provide new constraints on element recycling in subduction zones. We show that minor and accessory phases play a crucial role in controlling the concentration of key trace elements in subduction-zone fluids and that these phases are able to fractionate elements with similar chemical behaviour. We document element enrichment and trace element fractionation in the slab-derived fluid phase as a function of temperature. The results are compared to the composition of aqueous fluids in subducted sediments in order to address the question on how incompatible trace elements are released from the subducted slab.

2. Experimental

2.1. Piston-cylinder experiments

In order to study the trace element composition of subduction-zone fluids we performed piston-cylinder experiments on a trace element-doped starting gel with major elements (Table 1) similar to average Global Oceanic Subducted Sediments (GLOSS) (Plank and Langmuir, 1998) under fluid present conditions. The preparation of starting

Table 1
Starting material and comparison to selected sediment compositions, all on a volatile-free basis.

	EPSM	GLOSS	Marianas[a]		Tonga[a]		New Cal[b]
	SM	A	B	C	D	E	F
			Pel	Volc	Br. Clay	Ch/Clay	Pel
Major elements (wt.%)							
SiO_2	68.83	65.28	57.34	68.25	54.72	70.90	73.68
TiO_2	0.67	0.69	0.68	1.60	0.98	0.40	0.55
Al_2O_3	14.70	13.27	17.18	7.84	18.15	8.71	12.93
FeO	4.67	5.81	7.26	7.23	10.09	6.61	3.82
MnO	0.10	0.36	1.90	0.14	1.17	2.11	0.11
MgO	2.51	2.76	3.49	6.70	3.70	2.61	2.37
CaO	2.45	6.63	2.58	3.62	2.23	1.99	1.80
Na_2O	2.62	2.71	4.06	2.27	5.71	3.81	0.63
K_2O	2.94	2.27	4.38	2.05	2.86	1.88	3.97
P_2O_5	0.32	0.21	1.13	0.31	0.39	0.97	0.13
Total	99.81	100.00	100.00	100.00	100.00	100.00	100.00
Trace elements (ppm)							
Sc	56	15	20	9.1	23	21	14
Rb	225	64	104	26	46	35	56
Sr	215	364	219	267	2.38	216	163
Y	60	33	214	15	74	166	33
Zr	202	145	182	154	139	114	187
Nb	57	10	15	25	8.9	8.0	7.4
Cs	241	3.9	7.4	0.28	2.6	2.1	1.6
Ba	1170	865	356	134	381	1533	246
La	163	32	116	20	54	129	19
Ce	68	64	152	39	136	170	43
Nd	60	30	137	22	57	151	22
Sm	66	6.5	30	4.4	13	33	5.2
Eu	61	1.5	7.0	1.3	3.2	8.1	1.1
Gd	58	5.9	33	4.0	13	36	4.9
Dy	55	5.6	30	3.2	13	33	5.2
Er	57	3.3	20	1.5	7.9	19	3.4
Yb	60	3.1	15	1.3	7.4	16	3.9
Hf	48	4.5	4.7	4.1	4.0	3.3	4.9
Ta	57	0.7	0.90	1.8	0.58	0.52	0.48
Pb	213	22	52	2.8	144	134	9.6
Th	238	7.7	11	2.5	13	9.0	6.9
U	532	1.9	2.2	0.45	2.2	1.2	2.4

[a] Data of oceanic sediments from Plank and Langmuir (1998).
[b] Eclogite facies pelite 1008 from Spandler et al. (2003).