Available online at www.sciencedirect.com

ScienceDirect

Geochimica et Cosmochimica Acta 71 (2007) 1542–1552

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Chlorine in submarine volcanic glasses from the eastern Manus basin

W.D. Sun [a,b,*], R.A. Binns [c,g], A.C. Fan [a,d], V.S. Kamenetsky [e], R. Wysoczanski [f], G.J. Wei [a], Y.H. Hu [a], R.J. Arculus [c,*]

[a] *Key Lab of Isotope Geochronology and Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, P.O. Box 1131, Guangzhou 510640, PR China*
[b] *Max-Planck Institut f. Chemie, Postfach 3060, Mainz 55020, Germany*
[c] *Department of Earth and Marine Sciences, The Australian National University, Canberra, ACT 0200, Australia*
[d] *Department of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, PR China*
[e] *ARC Centre of Excellence in Ore Deposits and School of Earth Sciences, Private Bag 79, Hobart, Tasmania, Australia*
[f] *Institute for Research on Earth Evolution, JAMSTEC, 2-15 Natsushima-cho, Yokosuka, Kanagawa 237-0061, Japan*
[g] *CSIRO Exploration and Mining, North Ryde, NSW 1670, Australia*

Received 15 May 2006; accepted in revised form 4 December 2006; available online 16 December 2006

Abstract

Submarine volcanic glasses from the eastern Manus Basin of Papua New Guinea, ranging from basalt to rhyodacite, clarify the geochemical behavior of Cl in arc-type magmas. For the Manus samples, Cl is well correlated with non-volatile highly incompatible trace elements, suggesting it was not highly volatile and discounting significant seawater contamination. The Cl partition coefficient is close to but slightly lower than that of Nb and K_2O, a behavior similar to that in mid-ocean ridge basalts (MORB) and ocean island basalts (OIB). The similar incompatibilities of Cl and Nb imply that the Cl/Nb values of the eastern Manus Basin glasses reflect their magma source. For glasses from other west Pacific back-arc basins, Cl/Nb, Ba/Nb, and U/Nb increase towards the subduction trench, indicating increased contribution of a component enriched in Cl, Ba, and U, likely from subduction-released slab fluids. It is estimate that ~80% of the Cl in the Manus arc-type glasses was added directly from subducted slab-derived fluids. We have also modeled Cl behavior during magma evolution in general. Our results show that the behavior of Cl in magma is strongly influenced by pressure, initial H_2O content, and the degree of magmatic fractionation. At early stages of magmatic evolution, for magmas with initial H_2O content of <4.0 wt%, Cl is highly incompatible under all pressures. By contrast, for more evolved magmas at moderately high pressure and high H_2O contents, considerable amounts of Cl can be extracted from the magma once H_2O saturation is reached. Accordingly, Cl is usually highly incompatible in MORB and OIB because of their low H_2O contents and relatively low degrees of fractional crystallization. The behavior of Cl in arc magmas is more complicated, ranging from highly incompatible to compatible depending on H_2O content and depth of magma chambers. The behavior of Cl in the eastern Manus Basin magmas is consistent with low H_2O contents (1.1–1.7 wt%) and evolution at low pressures (<0.1 GPa). Modeling results also indicate that Cl will behave differently in intrusive rocks compared to volcanic rocks because of the different pressures involved. This may have a strong influence on the mechanisms of ore genesis in these two tectonic settings.

---

[*] Corresponding authors. Fax: +86 20 85291510.
E-mail addresses: weidongsun@gig.ac.cn (W.D. Sun), rarculus@ems.anu.edu.au (R.J. Arculus).

doi:10.1016/j.gca.2006.12.003

1. INTRODUCTION

The behavior of Cl in magmatic systems can potentially allow us to trace the nature of source inputs, fractional crystallization processes, and history of volatile phase separation events. For example, Cl can behave as a volatile element, and as such may provide insights into the degassing and recycling processes of the mantle (Lassiter et al., 2002). Chloride is mobile during subduction (Kent et al., 2002), as shown by significantly higher Cl concentrations in melt inclusions and submarine volcanic glasses from backarc basins (Harris and Anderson, 1984; Kamenetsky et al., 1997; Kent et al., 2002; Wallace, 2005) compared with uncontaminated MORB and OIB (Lassiter et al., 2002; Saal et al., 2002; Stroncik and Haase, 2004), as well as high Cl contents in fluid inclusions in ecologites (Philippot et al., 1998; Fu et al., 2000; Xiao et al., 2000; Scambelluri and Philippot, 2001; Xiao et al., 2002). Therefore, Cl is believed to be a good tracer for studies of subduction processes as well as the fate of recycled oceanic slabs (Stroncik and Haase, 2004). Importantly, experiments have shown that Cl can strongly affect the solid–fluid partitioning of many elements, ranging from K, Na, Cs, Ba, Pb, Zn, Cu, Mo, Au, Ag, U, and Th, rare earth elements (REE), to platinum group elements (PGE) (Keppler and Wyllie, 1990, 1991; Brenan and Watson, 1991; Brenan et al., 1994; Ayers and Eggler, 1995; Brenan et al., 1995a,b; Keppler, 1996; Gammons et al., 1997; Xiao et al., 1998; Herzarkhani et al., 1999; Archibald et al., 2001; Allen and Seyfried, 2005). Therefore the behavior of Cl is very important for the mobility of these elements during subduction and their geochemical behavior in magmatism as well as subsequent mineralisation processes. Furthermore, Cl is abundant in seawater, such that it is sensitive to melt/crust and melt/hydrosphere interaction (Magenheim et al., 1995; Michael and Cornell, 1998; Kent et al., 1999a,b; Lassiter et al., 2002). Despite all of these useful behaviors, our detailed knowledge is still limited by the lack of adequate data of the abundance systematics of Cl during magmatic evolution.

In this contribution, we have determined Cl abundances as well as major and other trace element compositions of volcanic glasses from the eastern Manus Basin to investigate the behavior of Cl during the evolution of these backarc basin magmas and those of arcs more generally.

2. SAMPLES AND RESULTS

2.1. Samples

The Manus Basin in the southwestern Pacific is an actively spreading backarc basin surrounded by the islands of New Britain, New Ireland, New Guinea and Manus, bounded to the north by the now inactive Manus Trench and to the south by the New Britain Arc and associated trench (Taylor, 1995; Taylor and Martinez, 2003) (Fig. 1). The locations of the samples can be found in (Sun et al., 2004a). The eastern Manus Basin is believed to have been located above subduction zones for more than 40 Ma (Exon et al., 1986; Kamenetsky et al., 2001). The rock types of the whole Manus basin range from MORB-type to arc-type (Woodhead and Johnson, 1993; Woodhead et al., 1998; Sinton et al., 2003; Taylor and Martinez, 2003; Woodhead and Brauns, 2004), with active hydrothermal systems and mineralisation (Yang and Scott, 1996; Moss et al., 2001; Binns et al., 2002a,b; Yang and Scott, 2002; Sun et al., 2004a). The studied set of submarine (1640–2000 m water depth) quenched glasses from the eastern Manus Basin region are arc-type magmas, ranging from basalt to rhyodacite, and have the typical low Nb/U and high Pb/Ce signatures of arc magmas. The coherency of trace element and isotopic signatures are consistent with formation via a single magmatic fractionation series (Yang and Scott, 2002) and/or derivation from a common mantle source (Sun et al., 2003b, 2004a).

2.2. Methods and results

Major element analysis of glasses was performed using the JEOL Superprobe JXA-8200 electron microprobe (Max Planck Institute for Chemistry, Mainz, Germany). We applied 15 kV accelerating voltage, 12 nA electron beam current and defocused to 5 μm size beam for analyses

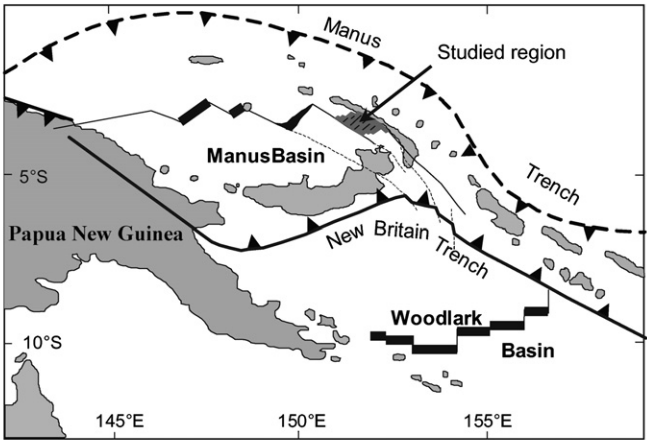

Fig. 1. Geological sketch map of the Manus Basin modified after Binns (Binns and Scott, 1993; Binns et al., 2002a,b), showing the location of the studied arc-type volcanic glasses and surrounding tectonic environments.

of glasses and olivine-hosted glass inclusions. Peak counting times on major elements were 60 and 30 s of background. The ZAF correction routine was used. A set of reference materials (i.e. natural and synthetic oxides, minerals, and glasses; Micro-Analysis Consultants Ltd, Cambridgeshire, UK) and the Smithsonian Institution standard set for electron microprobe analysis were used for routine calibration and instrument stability monitoring. Typical analytical uncertainties ($2RSD = 2\sigma$ relative standard deviation) are 1.4–2.8% for SiO_2, Al_2O_3, FeO, MgO, CaO, TiO_2; 5.6% for Na_2O, 10% for K_2O, 16% for P_2O_5, and 32% for MnO. As a monitor sample to control precision and accuracy of Cl measurements, we used the USNM 111240/52 VG-2 basaltic glass (recommended values of 0.030 wt% Cl). The concentration of 0.029 ± 0.007 wt% ($\pm 2\sigma$) were obtained for Cl during this study. Water contents were analyzed in the Institute for Research on Earth Evolution, JAMSTEC, Japan using FTIR. Water species calculated from either Mid-IR FTIR spectra (H_2O_{tot} peak at 3550 cm^{-1}, H_2O_{mol} at 1615 cm^{-1}) or Near-IR FTIR spectra (H_2O_{mol} at 5200 cm^{-1}, OH- at 4500 cm^{-1}), depending on most suitable intensities. Detailed procedure has been describe (Wysoczanski and Tani, 2006).

Trace elements were analyzed using laser ablation ICP-MS at the Research School of Earth Sciences, Australian National University. NIST 612 was used as the external standard and ^{43}Ca was used as an internal standard (Eggins et al., 1998a,b; Eggins and Shelley, 2002; Sun et al., 2003a). The reference values for major and trace elements in NIST 612 were from (Pearce et al., 1997). BCR-2g was used as a second standard to check the data quality during the analyses. All trace elements were analyzed using a spot size of 100 μm in diameter and a laser repetition rate of 5 Hz. The results are shown in Table 2.

3. COMPATIBILITY OF CL IN MANUS BASIN ARC MAGMAS

Overall Cl concentrations in the investigated samples are high and increase with increasing SiO_2 contents (Table 1). Remarkably, Cl is well correlated with non-volatile, highly incompatible elements. For example, the log(Cl) is positively correlated with log(K_2O) (Fig. 2), with a correlation coefficient of $R^2 = 0.96$. The slope of the log(Cl) versus log(K_2O) correlation is 0.977, indicating that Cl is very close to but slightly more incompatible than K. Consistently, the log(Cl) is also highly correlated with log(Nb), log(Ta), log(U), and log(Th), with very good correlation coefficients ($R^2 \sim 0.96$) (Fig. 3). These results suggest Cl was not volatile and that there was no significant seawater contamination or crustal assimilation during the evolution of the eastern Manus Basin magmas.

The behavior of Cl observed in this study is unlike that predicted based on experiments at 0.2 GPa, which show a dramatic reduction in Cl solubility during the chemical evolution of magmas ranging from diorite to quartz monzonite

Table 1
Chlorine and major element concentrations for arc-type glasses from the eastern Manus Basin

Operation	Sample No.[a]	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O[b]	K_2O	P_2O_5	Cl	H_2O	Total[d]
MD-3	107094	51.76	0.41	14.80	7.91	0.15	7.83	12.35	1.99	0.24	0.06	0.11	1.23	97.62
MD-101A	134043A	52.30	0.42	15.54	7.98	0.16	7.01	11.56	1.96	0.31	0.08	0.09		97.40
MD-101B	134043B	52.83	0.48	15.10	8.97	0.18	6.59	10.83	2.03	0.35	0.08	0.11		97.56
100DR	118935	54.18	0.54	15.82	7.46	0.14	5.60	9.50	2.75	0.66	0.15	0.23	1.30	97.05
Dive 299-1	132122	54.82	0.95	14.48	10.72	0.17	4.16	7.57	3.39	0.71	0.25	0.24		97.48
86DR	118856	55.42	0.78	15.08	9.59	0.17	4.27	8.06	3.07	0.69	0.19	0.30	1.40	97.62
MD-7	107243	56.83	1.07	14.24	10.00	0.19	2.99	6.21	3.00	0.84	0.42	0.30	1.37	96.09
MD-53B	132253	59.45	0.97	15.32	8.17	0.18	2.37	5.66	3.21	0.91	0.37	0.31	1.51	96.93
MD142	142490	60.73	1.01	15.10	7.75	0.17	2.26	5.66	3.63	0.96	0.55	0.34		98.19
MD-53A	132273	63.81	0.82	14.77	5.77	0.19	1.66	4.34	2.83	1.16	0.27	0.39	1.61	96.02
MD94	133818A	65.04	0.67	13.79	5.89	0.18	1.25	3.93	3.44	1.13	0.28	0.30		95.91
MD-36	118483	66.14	0.68	14.25	4.89	0.15	0.96	3.22	3.04	1.50	0.19	0.49	1.66	95.52
MD-114	134306	66.21	0.72	14.65	5.01	0.15	1.14	3.52	3.05	1.38	0.20	0.45	1.67	96.48
MD-28	118349	66.42	0.65	14.15	4.86	0.14	1.42	3.46	2.68	1.34	0.15	0.42	1.64	95.69
MD57	132385A	66.46	0.65	14.10	4.96	0.16	1.45	3.52	3.63	1.37	0.16	0.44		96.90
MD-65	132496	66.98	0.65	14.31	5.02	0.13	1.50	3.60	3.24	1.40	0.14	0.43		97.40
MD103	134104	67.22	0.66	14.27	4.99	0.15	1.59	3.74	3.68	1.37	0.16	0.43		98.25
MD110	134199	67.39	0.66	14.24	5.00	0.16	1.63	3.69	3.52	1.41	0.16	0.43		98.29
MD136	142404	68.32	0.76	12.79	4.96	0.17	0.72	2.53	3.42	1.64	0.17	0.53		96.01
134729	134729	68.93	0.56	13.14	3.89	0.13	0.36	2.06	3.71	1.93	0.10	0.66		95.49
MD111	134213	71.01	0.67	13.59	3.89	0.07	0.43	2.31	3.81	1.77	0.14	0.55		98.24
MD141 MI-2[c]	142484 MI-2	71.47	0.39	12.53	3.94	0.08	0.25	1.75	3.30	1.95	0.08	0.72		96.46
MD141 MI-1[c]	142484 MI-1	71.60	0.44	12.45	3.94	0.08	0.24	1.73	3.11	1.79	0.02	0.66		96.08
MD-39	118497	72.53	0.38	12.33	2.98	0.04	0.12	1.24	2.59	2.20	0.05	0.76	1.24	95.24
87DR	118866	72.80	0.40	12.62	2.98	0.13	0.33	1.77	2.60	1.71	0.05	0.76	1.20	96.14
MD-6	107162	74.76	0.34	11.06	2.84	0.06	0.14	0.98	2.44	2.19	0.04	0.84	1.11	95.69
MD141	142484	75.03	0.34	10.94	2.94	0.11	0.13	0.89	3.09	2.49	0.05	0.81		96.81

Note. [a]CSIRO collection; [b]Na_2O contents are systematically lower than XRF results due to the high beam current; [c]Melt inclusions; [d]Without water.

Table 2
Chlorine and trace elements concentrations of arc-type glasses from the eastern Manus Basin (μg/g)

Operation	Sample No.	Cu[a]	Nb	Ba	Ta	Pb	Th	U	Re[a]	Au[a]	Cl (wt%)
MD6	107162	17.2	2.30	464	0.15	7.19	1.65	1.07	1.12	1.59	0.84
MD6		16.8	2.15	470	0.13	6.76	1.56	1.03	1.08	1.43	
MD6		16.5	2.22	461	0.15	6.93	1.57	1.04	1.04	1.38	
MD39	118497	17.9	2.09	476	0.13	7.90	1.60	1.07	1.06	1.23	0.76
MD39		33.9	2.12	473	0.13	7.56	1.61	1.04	1.08	0.89	
MD39		23.5	2.04	455	0.13	7.20	1.46	0.96	1.09	1.06	
87DR	118866	16.0	2.20	418	0.13	6.53	1.46	0.95	2.78	3.70	0.76
87DR		17.2	2.26	441	0.14	6.65	1.49	0.97	41.0	73.5	
87DR		18.3	2.35	437	0.14	6.77	1.50	0.99	0.91	3.81	
MD28	118349	19.8	1.64	318	0.10	5.36	1.04	0.66	1.42	1.34	0.42
MD28		20.0	1.71	325	0.11	5.56	1.08	0.66	1.38	1.42	
MD28		18.9	1.64	327	0.10	5.39	1.07	0.67	1.45	1.30	
MD65	132496	19.3	1.58	319	0.09	5.44	1.06	0.65	1.07	0.80	0.43
MD65		18.2	1.64	320	0.09	5.37	1.07	0.66	1.19	1.08	
MD65		19.2	1.66	316	0.10	5.38	1.05	0.66	1.17	0.87	
MD114	134306	28.1	1.73	322	0.11	5.41	1.04	0.65	1.54	3.41	0.45
MD114		43.4	1.71	319	0.10	5.30	1.02	0.66	1.70	3.09	
MD114		30.3	1.72	328	0.11	5.39	1.05	0.68	1.49	3.44	
MD36	118483	28.9	1.42	273	0.09	4.56	0.85	0.54	1.99	2.36	0.49
MD36		24.4	1.51	310	0.10	5.24	0.96	0.64	1.73	1.32	
MD36		27.0	1.41	268	0.08	4.42	0.83	0.53	1.87	2.37	
MD53A	132273	30.7	1.23	251	0.09	4.13	0.73	0.48	3.06	4.22	0.39
MD53A		32.1	1.40	274	0.09	4.47	0.82	0.51	1.61	4.37	
MD53A		28.2	1.36	266	0.08	4.51	0.81	0.51	1.74	2.13	
MD53B	132253	34.6	0.98	208	0.07	3.56	0.61	0.39	2.66	1.22	0.31
MD53B		50.2	1.14	224	0.07	4.30	0.70	0.44	2.99	1.51	
MD53B		33.8	1.10	228	0.08	3.93	0.70	0.44	3.18	1.27	
MD7	107243	264	0.96	196	0.07	3.26	0.55	0.36	2.34	7.00	0.30
MD7		234	0.89	186	0.06	3.10	0.54	0.34	2.25	7.84	
86DR	118856	201	0.75	169	0.05	2.93	0.49	0.31	1.26	7.24	0.30
86DR		199	0.76	175	0.04	3.03	0.51	0.31	1.14	7.70	
86DR		189	0.80	178	0.05	3.06	0.51	0.35	1.24	7.61	
100DR	118935	84.1	0.69	172	0.04	2.80	0.44	0.30	1.11	3.49	0.23
100DR		82.9	0.67	179	0.04	2.97	0.47	0.31	1.12	3.53	
100DR		76.7	0.73	175	0.04	2.85	0.43	0.28	1.08	3.31	
MD101A	134043A	117	0.26	79.5	0.02	1.63	0.20	0.12	0.83	5.54	0.09
MD101A		92.5	0.22	66.1	0.01	1.34	0.15	0.11	0.76	4.59	
MD101A		116	0.29	77.7	0.01	1.54	0.19	0.12	0.61	4.06	
MD101B	134043B	135	0.43	121	0.03	2.58	0.27	0.19	0.83	6.06	0.11
MD101B		117	0.40	108	0.02	2.17	0.26	0.17	0.66	4.49	
MD101B		113	0.38	107	0.03	2.15	0.24	0.16	0.75	5.06	
MD3	107094	101	0.33	79.0	0.02	1.35	0.16	0.10	0.70	3.84	0.11
MD3		103	0.32	79.4	0.02	1.41	0.15	0.10	0.78	4.34	
MD3		104	0.33	80.9	0.02	1.42	0.16	0.10	11.8	31.3	

Note. [a] Cu, Re and Au were determined using larger spots size and faster repetation rates, the average values were published in (Sun et al., 2003b, 2004a,b), oxide interferences on Re and Au were corrected (Sun et al., 2003a, 2004a).

in composition (Webster et al., 1999; Webster, 2004), implying the eastern Manus Basin magmas probably evolved at different pressures or Cl is far below saturation.

log(A)–log(B) diagrams are useful to compare the compatibility of two elements, A and B (Jochum et al., 1993; Jochum and Hofmann, 1997; Hofmann, 2003). For highly incompatible elements like Nb and U, the slope can be taken as the ratio between the partition coefficients of A and B. The results show that Cl is ~5% less incompatible than U and Th, and is ~1.5% and ~2% more incompatible than Nb and K, respectively, (Figs. 2–4) during the evolution of eastern Manus Basin magmas. In this respect, our results are consistent with experiments at relatively low pressures, which suggests that Cl is highly soluble in basaltic melts with relatively low H_2O contents (<3–4 wt%) (Webster et al., 1999).

Previous studies also suggest that Cl has the same incompatibility as K in MORB and OIB, based on the roughly constant Cl/K_2O values of ~0.04 for uncontaminated MORB and OIB magmas (Lassiter et al., 2002). In fact, the behavior of Cl is often masked by other effects. For example, samples contaminated by seawater and crust assimilation usually have varied and usually high Cl/K (Michael and Cornell, 1998; Lassiter et al., 2002), whereas

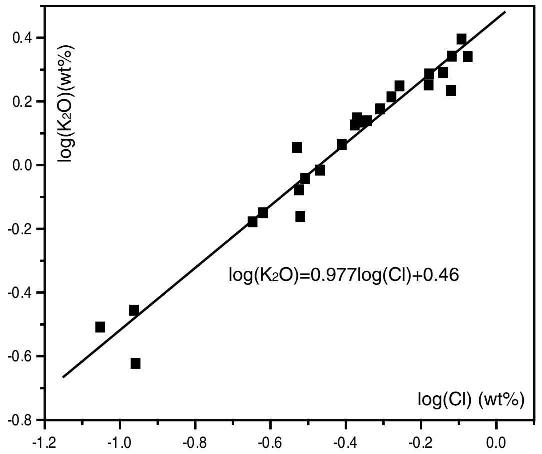

Fig. 2. Diagram of log(Cl) versus log(K_2O) for the eastern Manus Basin glasses. The good correlation is consistent with the hypothesis that the glasses are representative of one magmatic fractionating series (Yang and Scott, 2002) or come from a common mantle source (Sun et al., 2003b, 2004a).

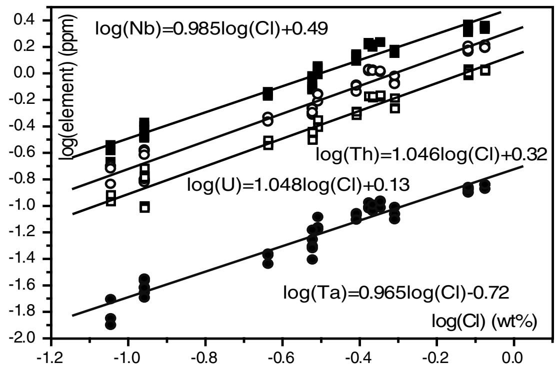

Fig. 3. Diagram of log(Cl) verusus log(Nb), log(Ta), log(U), and log(Th) for eastern Manus glasses. The slopes are all close to 1, indicating that Cl shares similar incompatibility to these other trace elements.

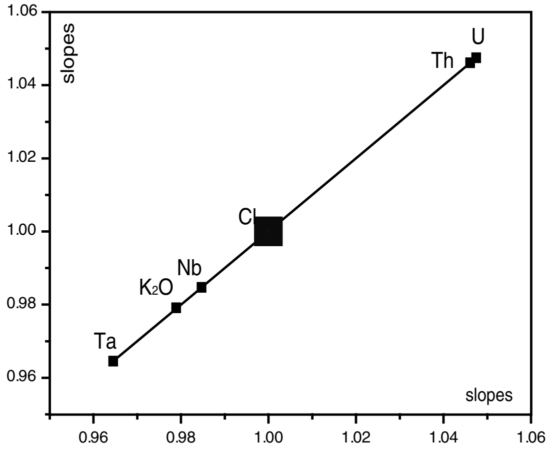

Fig. 4. Diagram of correlation slopes of Cl versus other highly incompatible elements (from Figs. 2 and 3) showing the relative incompatibility of Ta, K, Nb, U, and Th compared with Cl.

different mantle sources may also have different Cl/K (Stroncik and Haase, 2004). Given all these and that the arc-type magmas from the eastern Manus Basin are volatile-enriched compared with MORB, the similar compatibility of Cl in MORB and the eastern Manus Basin glasses seemingly indicates the compatibility of Cl might not change within the range of volatile contents exemplified by these magma types. It is worth noting the majority of MORB are saturated at eruption depths with a CO_2-dominated volatile phase (Saal et al., 2002). All eastern Manus Basin glasses are vesicular to varying extents, and were also volatile saturated at eruption depths with a volatile phase. We conclude that Cl was not highly volatile either before or during their eruption at sea floor depths ranging from 1640 to 2000 m.

4. VOLATILITY AND THE EFFECTS OF FLUIDS ON CHLORINE

The volatility of Cl depends on pressure, its chemical form, and H_2O content of the magmas. For example, HCl is highly volatile and is an important, highly reactive component in volcanic gases (Lowenstern, 1994; Symonds et al., 1994). In general, Cl is mainly present as NaCl and KCl in magmatic fluids, both of which are involatile as indicated by considerably lower Cl concentrations in vapor phases compared with those of coexisting brines (Cline and Bodnar, 1991), particularly at low pressures (Webster et al., 1999). For volcanic glasses, it is believed that Cl is essentially not volatile at water depths >400 m (Stroncik and Haase, 2004). These characteristics can explain the limited Cl loss and good correlations between Cl and non-volatile elements in Manus Basin arc-type magmas.

Experiments however, show that although Cl is usually incompatible with respect to crystallizing minerals, it can be partitioned into supercritical, magmatic hydrous fluids (and potentially associated brine-vapor pairs). Modeling suggests that once the magma is H_2O-saturated, a considerable amount of Cl can be extracted into hydrous fluids (Cline and Bodnar, 1991), depending on pressure etc. The extent of Cl losses to a fluid depends heavily on the pressure, the degree of magma fractionation, and initial H_2O content (Cline and Bodnar, 1991). In the eastern Manus Basin, chlorides and, sulphides of ore-forming metals such as copper, zinc, and iron in CO_2-rich gaseous bubbles both in melt inclusions trapped in the phenocrysts of the volcanic rocks, and in the matrix glass have been reported (Yang and Scott, 1996; Kamenetsky et al., 2001, 2002), indicating that Cl is indeed dissolved in hydrous fluids.

To understand the detailed behavior of fluids and Cl in the eastern Manus Basin glasses specially and in arc magmas generally, we modeled the Cl contents in magmas during fractional crystallization at different pressures and initial H_2O contents (Fig. 5), using equations for H_2O solubility in magmas and Cl partition coefficients between magmas and fluids from the literature (Burnham, 1975; Shinohara et al., 1989; Cline and Bodnar, 1991). The results are compatible with previous modeling results on the salinity of aqueous fluids: higher pressures favor more Cl in any exsolved fluid, and higher pressures delay H_2O saturation

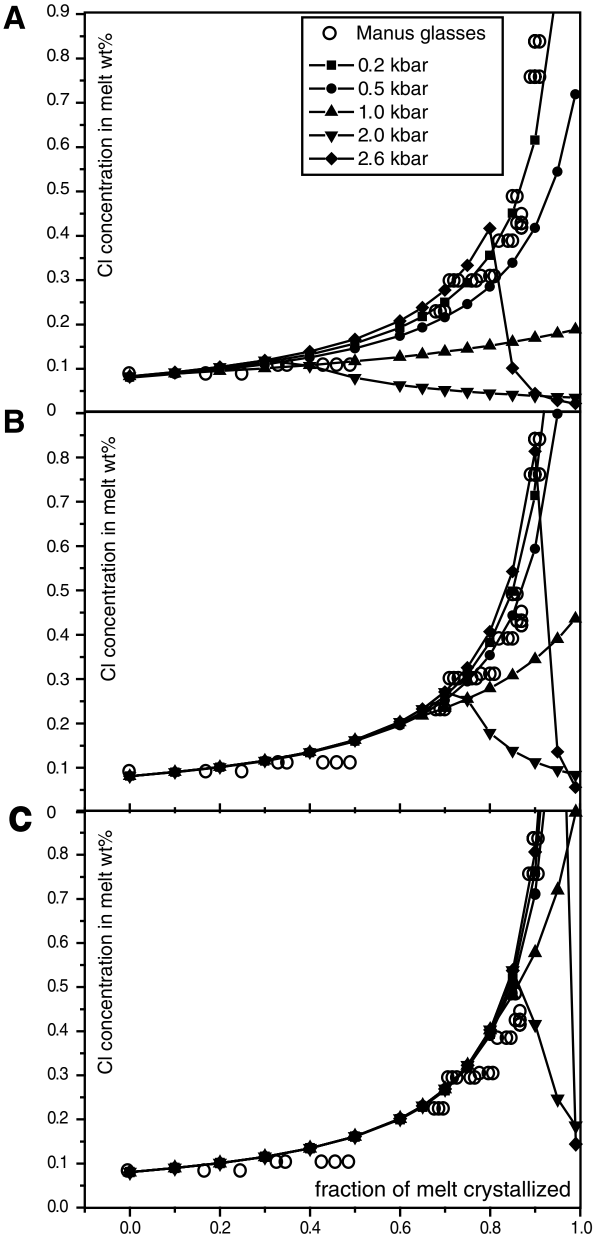

Fig. 5. Modeling of Cl concentrations in magma during fractional crystallization. Initial H_2O contents used are 4.0 wt% (A), 1.7 wt% (B), and 0.8 wt% (C) and initial Cl contents of 0.09 wt%, assuming anhydrous crystallizing minerals. Also shown are the observed Cl abundances in eastern Manus Basin samples. The degree of fractional crystallization was estimated using the Nb concentrations, assuming the most mafic sample represents the parental magma, and a partition coefficient for Nb = 0.01.

during crystallization (Cline and Bodnar, 1991; Bodnar, 1992). At the early stage of magma evolution, the Cl concentrations increase with fractional crystallization at all pressures and H_2O contents (Fig. 5). As fractional crystallization progresses, Cl concentrations in magmas become very sensitive to pressure and initial H_2O contents. For a magma with initial H_2O contents of 4.0 wt%, the critical pressure is ~0.1 GPa (Fig. 5A). At pressures <0.1 GPa, aqueous fluids exsolve from the magmas early, and Cl concentrations in melt continuously increase during magmatic evolution. At further lower pressures (e.g., 0.05 GPa), Cl concentrations increase rapidly at large degrees of fractional crystallization (>80%). In contrast, at moderately higher pressures (~0.2 GPa), aqueous fluid segregation occurs at progressively higher percentages of fractional crystallization. In this case, the Cl concentrations in magmas decrease once fluids appear, and within this pressure range the higher the pressure, the more rapidly the Cl content in the magma decreases (Fig. 5). When the pressure is high enough (e.g., 0.3 GPa for an initial H_2O content of ~1.7 wt% or less), no fluids exsolve from the magmas during evolution, and thus Cl mainly stays in melt again (Fig. 5). This is certainly not the case for the eastern Manus Basin, where abundant fluid inclusions have been observed (Kamenetsky et al., 2001, 2002).

The Manus samples are also plotted in Fig. 5, where the degree of fractional crystallization was estimated using the Nb concentrations and assuming the most mafic sample represents a primitive magma. Given the most mafic sample is probably parental rather than primitive, the degree of fractional crystallization is probably underestimated. Nonetheless, this will not change the overall evolution trend of Cl.

The evolution trend of arc-type glasses from the eastern Manus Basin is similar to relatively low pressure processes (Fig. 5). For an initial H_2O content of 4.0 wt% (Fig. 5A), the pressure of fractional crystallization should be as low as 0.02 GPa, whereas for an initial H_2O content of 1.7 wt%, the pressure should be ~0.05 GPa (Fig. 5B). Even for a lower initial H_2O content of 0.8 wt%, the required maximum pressure is still <0.1 GPa (Fig. 5C). The water contents of eastern Manus samples range from 1.11 to 1.67 wt% (Table 1), such that the pressure should be slightly higher than 0.05 GPa, but lower than 0.1 GPa (Fig. 5B). Eruption water depths in the eastern Manus Basin range from 1640 to 2000 m, corresponding to pressures of ~0.02 GPa. Therefore the magma chamber of the eastern Manus Basin samples is likely located a depth of ~2 km beneath the sea floor.

In summary, the behavior of Cl is strongly dependent on the pressure, the fractionation and the initial H_2O content of the magmas (Fig. 5). At the early stage of magmatic evolution, (e.g, for basaltic rocks), Cl stays in the melt under essentially all pressures for magmas with initial H_2O contents <4.0 wt% (Fig. 5). Given the H_2O contents of MORB (Saal et al., 2002) and OIB (Hauri, 2002) are usually much lower than arc volcanic glasses (e.g., <0.8 wt%) (Sobolev and Chaussidon, 1996), and that MORB and OIB are usually not as evolved as arc rocks, the observed highly incompatible character of Cl in MORB (Schilling et al., 1980) and OIB (Lassiter et al., 2002) is likely to be a general phenomenon. In contrast, arc rocks are usually more evolved and have high H_2O contents (Sobolev and Chaussidon, 1996), therefore the behavior of Cl should vary greatly. In particular, Cl should behave significantly different in intrusive rocks (formed at relatively high pressures) compared with volcanic rocks (Cline and Bodnar, 1991). This should have a strong influence on the behavior of Cl as well as the fluids, and is important for understanding the different mechanisms of ore genesis, e.g., the formation of Cu–Au ore deposits (Cline and Bodnar, 1991), in the two systems.

5. ADDITION OF CHLORINE TO ARC MAGMAS FROM SUBDUCTION-RELEASED FLUIDS

The Cl concentrations in magmas from back-arc basins are likely to be influenced by many different factors (Kent et al., 2002). Partitioning of Cl into aqueous fluids and vapor phase aside, the concentration of Cl within the mantle source, addition of Cl from subduction-released fluids, and shallow assimilation of the Cl-enriched materials during magma transportation as well as magma evolution are all believed to be important for understanding Cl in magmas from back-arc basins (Kent et al., 2002). Plots of Cl/K_2O and Cl/TiO_2 versus Ba/Nb have been successfully used to identify the contributions from seawater contamination and slab-derived fluids (Kent et al., 2002). These plots however, were not designed to quantify the contributions of these two components. First, K is one of the most mobile elements, similar to Rb and Ba (Pearce and Peate, 1995). It is estimated that 90–95% of the K in the oceanic crust is lost during dehydration (Becker et al., 2000). Moreover, the mobility of K is different from that of Cl because the former is mainly controlled by phengite stability (particularly at high pressures), which is subductable to depths of 70–300 km depending on the geotherm (Schmidt and Poli, 1998). In contrast, Cl is likely to be hosted mainly by Cl-rich minerals such as amphibole (Xiao et al., 2005), which is eliminated earlier than phengite during subduction (Xiong et al., 2005). In addition, a considerable amount of Cl may be recycled into the mantle as fluid inclusions in stable minerals. Therefore Cl/K_2O value is not a good quantitative proxy for the mobility of Cl. In the case of Cl/TiO_2, because Cl behaves similarly to Nb, which is considerably more incompatible than Ti (Sun and McDonough, 1989), Cl/TiO_2 changes during magmatic evolution and thus is not the best proxy for quantifying the contribution of Cl from subduction-released fluids. The different incompatibility of Cl and TiO_2 is probably a reason for the distinctively higher Cl/TiO_2 in the lower MgO samples (evolved) from central lau spreading center (CLSC) (Kent et al., 2002).

The mobility of Cl during subduction could be better tested using Cl/Nb values because Nb is one of the most conservative elements during subduction (McCulloch and Gamble, 1991; Pearce and Peate, 1995). Given the similar incompatibility of Cl and Nb and the constancy of the Cl/Nb of the glasses, this ratio should be characteristic of the source(s) of the magmas. For these reasons, the Cl/K_2O and Cl/TiO_2 versus Ba/Nb diagrams have been refined using plots of Cl/Nb versus Ba/Nb and U/Nb (Fig. 6).

To a first approximation, the arc-type samples show kind of "correlations" between Cl/Nb and Ba/Nb or U/Nb similar to those in Cl/K_2O and Cl/TiO_2 versus Ba/Nb diagrams (Kent et al., 2002). In detail however, there seem to be three trends in the Cl/Nb versus Ba/Nb diagram: the best one is defined by glasses from the eastern Manus Basin and Valu Fa (K) ridges (Fig. 6), whereas the west and east seamounts in the vicinity of the Valu Fa are offset. These three "trends" are likely due to different Cl/Nb in the parental magmas, which can be explained by three end-member mixing: the depleted mantle (plotting towards the bottom left hand corner of Fig. 6 A), a Cl-, Ba-, U-enriched component (top right) and a Cl-rich, Ba-, U-poor component (top left). The Cl/Nb, Ba/Nb and U/Nb values decrease from east seamount of the Valu Fa Ridge to Lau Spreading samples, indicating an increasing contributions from the Cl-, Ba-, U-enriched component towards the subduction zone (Fig. 6). Melt inclusions from the east and west seamounts (Kamenetsky et al., 1997) also point roughly to the same end-member with high Cl/Nb, Ba/Nb, and U/Nb. The most likely candidate for such a Cl-, Ba-,

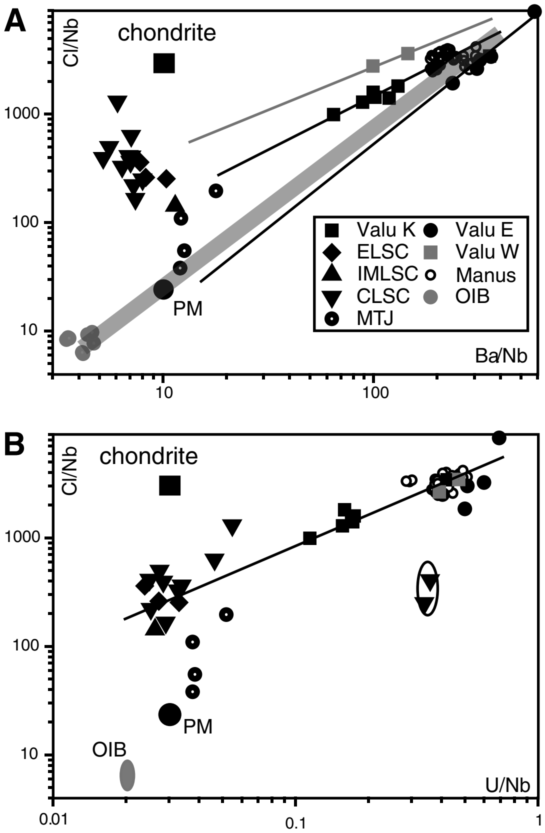

Fig. 6. Logarithm scale diagrams of Ba/Nb (A) and U/Nb (B) versus Cl/Nb for back-arc basin glasses and melt inclusions. Lau Basin Cl and trace element data are from (Kamenetsky et al., 1997; Kent et al., 2002), with additional trace element data from (Danyushevsky et al., 1993; Bach et al., 1998; Peate et al., 2001; Sun et al., 2003a, 2004b). Also plotted are OIB samples that were not contaminated by assimilation (Lassiter et al., 2002). ELSC, Eastern Lau Spreading Center; CLSC, Central Lau Spreading Center; IMLSC, Intermediate Lau Spreading Center; MTJ, Mangatolu (King's) Triple Junction (Kent et al., 2002; Sun et al., 2003a); Valu K, Valu Fa Ridge from (Kent et al., 2002); Valu E and W, eastern and western seamounts of the Valu Fa Ridge, respectively, (Kamenetsky et al., 1997; Sun et al., 2004b). The Ba/Nb, U/Nb and Cl/Nb decrease with decreasing distance towards the subduction, in the order of Valu E, Valu K, ELSC, IMLSC, and CLSC.

U-enriched component is subduction-released fluid (Kent et al., 2002).

The average Cl/Nb for eastern Manus Basin samples is 3200, which is considerably higher than primitive mantle (~26) (McDonough and Sun, 1995). Because Cl and Nb have similar incompatibilities, the Cl/Nb of the depleted mantle should be close to 26 if there was no other process that fractionated Cl from Nb. Assuming all additional Cl in arc magmas comes from the slab, then 99% of the Cl in eastern Manus Basin arc-type glasses is from subduction-released fluids. Such an assumption is not likely to be realistic because some Cl might also come from sources in the back arc basin crust via assimilation of seawater-derived Cl-rich material (Kent et al., 2002). This is supported by the fact that Cl/Nb varies significantly at the left side of Fig. 6 and, that most of the "correlation lines" in Cl/Nb versus Ba/Nb or U/Nb do not go through the primitive mantle (PM) (Valu E, Fig. 6).

As for the source of this Cl-rich, Ba-, U-poor component, the most likely candidates are brine-impregnated back-arc basin crust and seawater (Lassiter et al., 2002). The Cl/Nb varies substantially, with larger variations for the CLSC glasses (from ~100 to more than 1000) (Fig. 6), indicating a considerable amount of Cl in the CLSC and probably also in the ELSC was derived from a Cl-rich, Ba-, U-poor component. This is consistent with previous results: highly varied Cl/K_2O and Cl/TiO_2 coupled with MORB-like Ba/Nb for glasses from the ELSC and CLSC (Kent et al., 2002). These have been interpreted to reflect assimilations of oceanic crust or seawater based on the minimal slab input (as indicated by low Ba/Nb) and varied Cl and Cl/Nb ratios for these samples (Kent et al., 2002), comparable to those observed in MORB and OIB (Michael and Schilling, 1989; Kent et al., 1999a,b; Lassiter et al., 2002). Oceanic crusts are usually enriched in U through seawater hydrothermal alteration (Hart and Staudigel, 1982). In the Cl/Nb versus U/Nb diagram (Fig. 6B), most of the samples fall roughly in a line, with the exception of two samples from the CLSC and glasses from the Mangatolu Triple Junction (MTJ), suggesting that either the assimilated crust has low U, or seawater was the main process that resulted in the varied Cl/Nb. The two CLSC samples have considerably higher U/Nb compared to other CLSC glasses with similar Ba, implying that these samples might have gained U through seawater alteration or other processes. MTJ glasses fall close to the primitive mantle and OIB in Cl/Nb versus Ba/Nb, U/Nb diagrams (Fig. 6), indicating less effect from crustal assimilation and subduction-derived fluids. Dehydration of serpentinized mantle peridotite is potentially a major source of aqueous fluids in subducting slabs (Straub and Layne, 2003). Experiments show however, that fluids released from serpentinite breakdown usually contain high Ba (Tenthorey and Hermann, 2004), and therefore serpentinite-derived fluids seems unlikely as a source of the Cl-rich, Ba-, U-poor component.

Base on above discussions, we can return to the issue of how much Cl in the Manus glasses is derived from the presently subducting slab. Given the average Cl/Nb of the CLSC and ELSC is about 400 and assuming this represents the effect of the Cl-rich, Ba-, U-poor component (likely to be seawater derived as previously suggested (Kent et al., 2002)), then ~80% of the Cl in the Manus glasses could be derived directly from subduction-released fluids.

6. CONCLUSIONS

Chlorine is well correlated with highly incompatible elements, suggesting that there was minimal Cl loss during magmatic evolution and eruption of the quenched glasses in the eastern Manus Basin. The good correlations also indicate that Cl was highly incompatible during arc magma evolution, and that there was no obvious seawater contamination. The partition coefficient of Cl in eastern Manus Basin arc-type magmas is close to but slightly lower than that of Nb and K_2O, similar to that in mid-ocean ridge basalts (MORB) and ocean island basalts (OIB) (Lassiter et al., 2002). Calculation shows the behavior of Cl is strongly dependent on pressure, the initial H_2O content, and the extent of fractional crystallization of the magmas. The observed highly incompatible feature of Cl is consistent with shallow magma chambers and relatively low initial H_2O contents.

The Cl/Nb values of the glasses should be roughly constant during magma evolution because of the similar compatibilities of Cl and Nb, and thus represent the source character of the magmas.

Glasses from the eastern Manus Basin together with arc-type glasses from the Valu Fa Ridge (Kent et al., 2002) show roughly positive "correlations" between Cl/Nb and Ba/Nb, U/Nb, indicative of increasing contributions from a Cl-, Ba-, U-enriched component towards the subduction zone. The most likely candidate for such a component is subduction-released fluid. It is estimated that ~80% or more of the Cl in eastern Manus arc type magmas were derived from subduction-released fluids.

ACKNOWLEDGMENTS

We dedicate this paper to Dr. Shen-su Sun, who initiated this study with stimulating discussions and constructive suggestion, and helped to shape the findings reported here. This work was supported by the Nature Science Foundation of China (NSFC) (No. 40525010), Ministry of Science and Technology of China (No. 2006CB403505) and the Chinese Academy of Sciences to WDS. RAB was supported by CSIRO and a mineral company consortium, RJA and VSK were supported by the Australian Research Council.

REFERENCES

Allen D. E., and Seyfried W. E. (2005) REE controls in ultramafic hosted MOR hydrothermal systems: an experimental study at elevated temperature and pressure. *Geochim. Cosmochim. Acta* **69**(3), 675–683.

Archibald S. M., Migdisov A. A., and Williams-Jones A. E. (2001) The stability of Au-chloride complexes in water vapor at elevated temperatures and pressures. *Geochim. Cosmochim. Acta* **65**(23), 4413–4423.

Ayers J. C., and Eggler D. H. (1995) Partitioning of elements between silicate melt and H_2O–NaCl fluids at 1.5 and 2.0 GPa pressure—Implications for mantle metasomatism. *Geochim. Cosmochim. Acta* **59**(20), 4237–4246.

Bach W., Hegner E., and Erzinger J. (1998) Chemical fluxes in the Tonga subduction zone: evidence from the southern Lau Basin. *Geophys. Res. Lett.* **25**(9), 1467–1470.

Becker H., Jochum K. P., and Carlson R. W. (2000) Trace element fractionation during dehydration of eclogites from high-pressure terranes and the implications for element fluxes in subduction zones. *Chem. Geol.* **163**(1–4), 65–99.

Binns R. A., Barriga F. J. A. S., and Miller D. J. (2002a) Anatomy of an active felsic-hosted hydrothermal system, eastern Manus Basin. In *Proceeding of the Ocean Drilling Program*. Initial Reports, 193.

Binns R. A., McConachy T. F., Parr J. M., and Yeats C. J. (2002b) The PACMANUS Memoir (P2+). CSIRO Exploration and Mining, Report, 1032.

Binns R. A., and Scott S. D. (1993) Actively forming polymetallic sulfide deposits associated with felsic volcanic rocks in the eastern Manus back-arc basin, Papua New Guinea. *Econ. Geol.* **88**, 2226–2236.

Bodnar R. J. (1992) Can we recognize magmatic fluid inclusions in fossil systems based on room-temperature phase relations and microthermometric behavior? *Report of Geological Survey Japan* **279**, 26–30.

Brenan J. M., Shaw H. F., Phinney D. L., and Ryerson F. J. (1994) Rutile-aqueous fluid partitioning of Nb, Ta, Hf, Zr, U and Th—Implications for high-field strength element depletions in island arc basalts. *Earth Planet. Sci. Lett.* **128**(3–4), 327–339.

Brenan J. M., Shaw H. F., and Ryerson F. J. (1995a) Experimental evidence for the origin of lead enrichment in convergent margin magmas. *Nature* **378**(6552), 54–56.

Brenan J. M., Shaw H. F., Ryerson F. J., and Phinney D. L. (1995b) Mineral-aqueous fluid partitioning of trace elements at 900 degrees C and 2.0 GPa—Constraints on the trace element chemistry of mantle and deep-crustal fluids. *Geochim. Cosmochim. Acta* **59**(16), 3331–3350.

Brenan J. M., and Watson E. B. (1991) Partitioning of trace-elements between olivine and aqueous fluids at High P-T conditions—Implications for the effect of fluid composition on trace-element transport. *Earth Planet. Sci. Lett.* **107**(3–4), 672–688.

Burnham C. W. (1975) Water and magmas: a mixing model. *Geochim. Cosmochim. Acta* **39**, 1077–1084.

Cline J. S., and Bodnar R. J. (1991) Can economic porphyry copper mineralization be generated by a typical calc-alkaline melt. *J. Geophys. Res.-Solid Earth Planets* **96**(B5), 8113–8126.

Danyushevsky L. V., Falloon T. J., Sobolev A. V., Crawford A. J., Carroll M., and Price R. C. (1993) The H_2O content of basalt glasses from southwest Pacific back-arc basins. *Earth Planet. Sci. Lett.* **117**(3–4), 347–362.

Eggins S. M., Kinsley L. P. J., and Shelley J. M. G. (1998a) Deposition and element fractionation processes during atmospheric pressure laser sampling for analysis by ICP-MS. *Appl. Surf. Sci.* **129**, 278–286.

Eggins S. M., Rudnick R. L., and McDonough W. F. (1998b) The composition of peridotites and their minerals: a laser-ablation ICP-MS study. *Earth Planet. Sci. Lett.* **154**(1–4), 53–71.

Eggins S. M., and Shelley J. M. G. (2002) Compositional heterogeneity in NIST SRM 610-617 glasses. *Geostandard. Newslett.* **26**(3), 269–286.

Exon N. F., Stewart W. D., Sandy M. J., and Tiffin D. L. (1986) Geology and offshore petroleum prospects of the eastern New Ireland Basin, northeastern Papua New Guinea. *BMR J. Austr. Geol. Geophys.* **10**, 39–51.

Fu B., Xiao Y. L., Zheng Y. F., Touret J. L. R., van den Kerkhof A. M., and Hoefs J. (2000) Fluid inclusions in ultrahigh pressure metamorphic rocks from Shuanghe and Bixiling in Dabie Shan. *Acta Petrol. Sin.* **16**(1), 119–126.

Gammons C. H., Yu Y. M., and Williams-Jones A. E. (1997) The disproportionation of gold(I) chloride complexes at 25 to 200 °C. *Geochim. Cosmochim. Acta* **61**(10), 1971–1983.

Harris D. M., and Anderson A. T. (1984) Volatiles H_2O, CO_2, and Cl in a subduction related basalt. *Contrib. Mineral. Petrol.* **87**(2), 120–128.

Hart S. R., and Staudigel H. (1982) The control of alkalies and uranium in sea water by ocean alteration. *Earth Planet. Sci. Lett.* **58**, 202–212.

Hauri E. (2002) SIMS analysis of volatiles in silicate glasses, 2: isotopes and abundances in Hawaiian melt inclusions. *Chem. Geol.* **183**(1–4), 115–141.

Herzarkhani A., Williams-Jones A. E., and Gammons C. H. (1999) Factors controlling copper solubility and chalcopyrite deposition in the Sungun porphyry copper deposit, Iran. *Miner. Deposita* **34**(8), 770–783.

Hofmann A. W. (2003) Sampling mantle heterogeneity through oceanic basalts: isotopes and trace elements. In *Treatise of Geochemistry*, (ed. R. Carlson). , vol. 2, pp. 61–101. Elsevier.

Jochum K. P., and Hofmann A. W. (1997) Constraints on earth evolution from antimony in mantle-derived rocks. *Chem. Geol.* **139**(1–4), 39–49.

Jochum K. P., Hofmann A. W., and Seufert H. M. (1993) Tin in mantle-derived rocks—Constraints on earth evolution. *Geochim. Cosmochim. Acta* **57**(15), 3585–3595.

Kamenetsky V. S., Binns R. A., Gemmell J. B., Crawford A. J., Mernagh T. P., Maas R., and Steele D. (2001) Parental basaltic melts and fluids in eastern Manus backarc basin; implications for hydrothermal mineralisation. *Earth Planet. Sci. Lett.* **184**(3–4), 685–702.

Kamenetsky V. S., Crawford A. J., Eggins S. M., and Muehe R. (1997) Phenocryst and melt inclusion chemistry of near-axis seamounts, Valu Fa Ridge, Lau Basin; insight into mantle wedge melting and the addition of subduction components. *Earth Planet. Sci. Lett.* **151**(3–4), 205–223.

Kamenetsky V. S., Davidson P., Mernagh T. P., Crawford A. J., Gemmell J. B., Portnyagin M. V., and Shinjo R. (2002) Fluid bubbles in melt inclusions and pillow-rim glasses: high-temperature precursors to hydrothermal fluids. *Chem. Geol.* **183**(1–4), 349–364.

Kent A. J. R., Clague D. A., Honda M., Stolper E. M., Hutcheon I. D., and Norman M. D. (1999a) Widespread assimilation of a seawater-derived component at Loihi Seamount, Hawaii. *Geochim. Cosmochim. Acta* **63**(18), 2749–2761.

Kent A. J. R., Norman M. D., Hutcheon I. D., and Stolper E. M. (1999b) Assimilation of seawater-derived components in an oceanic volcano: evidence from matrix glasses and glass inclusions from Loihi seamount, Hawaii. *Chem. Geol.* **156**(1–4), 299–319.

Kent A. J. R., Peate D. W., Newman S., Stolper E. M., and Pearce J. A. (2002) Chlorine in submarine glasses from the Lau Basin: seawater contamination and constraints on the composition of slab-derived fluids. *Earth Planet. Sci. Lett.* **202**(2), 361–377.

Keppler H. (1996) Constraints from partitioning experiments on the composition of subduction-zone fluids. *Nature* **380**(6571), 237–240.

Keppler H., and Wyllie P. J. (1990) Role of fluids in transport and fractionation of uranium and thorium in magmatic processes. *Nature* **348**(6301), 531–533.

Keppler H., and Wyllie P. J. (1991) Partitioning of Cu, Sn, Mo, W, U, and Th between Melt and Aqueous Fluid in the Systems Haplogranite-H_2O HCl and Haplogranite-H_2O Hf. *Contrib. Mineral. Petrol.* **109**(2), 139–150.

Lassiter J. C., Hauri E. H., Nikogosian I. K., and Barsczus H. G. (2002) Chlorine-potassium variations in melt inclusions from Raivavae and Rapa, Austral Islands: constraints on chlorine recycling in the mantle and evidence for brine-induced melting of oceanic crust. *Earth Planet. Sci. Lett.* **202**(3–4), 525–540.

Lowenstern J. B. (1994) Chlorine, fluid immiscibility, and degassing in peralkaline magmas from Pantelleria, Italy. *American Mineral.* **79**(3-4), 353–369.

Magenheim A. J., Spivack A. J., Michael P. J., and Gieskes J. M. (1995) Chlorine stable-isotoep composition of the oceanic-crust: Implications for Earths distribution of chlorine. *Earth Planet. Sci. Lett.* **131**(3–4), 427–432.

McCulloch M. T., and Gamble A. J. (1991) Geochemical and geodynamical constraints on subduction zone magmatism. *Earth Planet. Sci. Lett.* **102**(3–4), 358–374.

McDonough W. F., and Sun S. S. (1995) The composition of the Earth. *Chem. Geol.* **120**(3–4), 223–253.

Michael P. J., and Cornell W. C. (1998) Influence of spreading rate and magma supply on crystallization and assimilation beneath mid-ocean ridges: Evidence from chlorine and major element chemistry of mid-ocean ridge basalts. *J. Geophys. Res.-Solid Earth* **103**(B8), 18325–18356.

Michael P. J., and Schilling J. G. (1989) Chlorine in mid-ocean ridge magmas: evidence for assimilation of seawater-influenced components. *Geochim. Cosmochim. Acta* **53**, 3131–3143.

Moss R., Scott S. D., and Binns R. A. (2001) Gold content of eastern Manus Basin volcanic rocks; implications for enrichment in associated hydrothermal precipitates. *Econ. Geol.* **96**(1), 91–107.

Pearce J. A., and Peate D. W. (1995) Tectonic implications of the composition of volcanic arc magmas. *Ann. Rev. Earth Planet. Sci.* **23**, 251–285.

Pearce N. J. G., Perkins W. T., Westgate J. A., Gorton M. P., Jackson S. E., Neal C. R., and Chenery S. P. (1997) A compilation of new and published major and trace element data for NIST SRM 610 and NIST SRM 612 glass reference materials. *Geostandard. Newsletter* **21**, 115–144.

Peate D. W., Kokfelt T. F., Hawkesworth C. J., Van Calsteren P. M., Hergt J. M., and Pearce J. A. (2001) U-series isotope data on Lau Basin glasses: The role of subduction-related fluids during melt generation in back-arc basins. *J. Petrol.* **42**(8), 1449–1470.

Philippot P., Agrinier P., and Scambelluri M. (1998) Chlorine cycling during subduction of altered oceanic crust. *Earth Planet. Sci. Lett.* **161**(1–4), 33–44.

Saal A. E., Hauri E. H., Langmuir C. H., and Perfit M. R. (2002) Vapour undersaturation in primitive mid-ocean-ridge basalt and the volatile content of Earth's upper mantle. *Nature* **419**(6906), 451–455.

Scambelluri M., and Philippot P. (2001) Deep fluids in subduction zones. *Lithos* **55**(1–4), 213–227.

Schilling J. G., Bergeron M. B., and Evans R. (1980) Halogens in the mantle beneath the North Atlantic. *Phil. Trans. R. Soc. Lond.* **297**, 147–178.

Schmidt M. W., and Poli S. (1998) Experimentally based water budgets for dehydrating slabs and consequences for arc magma generation. *Earth Planet. Sci. Lett.* **163**(1–4), 361–379.

Shinohara H., Iiyama J. T., and Matsuo S. (1989) Partition of chlorine compounds between silicate melt and hydrothermal solutions, I, Partition of NaCl-KCl. *Geochim. Cosmochim. Acta* **53**, 2617–2630.

Sinton J. M., Ford L. L., Chappell B. W., and McCulloch M. T. (2003) Magma genesis and mantle heterogeneity in the Manus back-arc basin, Papua New Guinea. *J. Petrol.* **44**(1), 159–195.

Sobolev A. V., and Chaussidon M. (1996) H_2O concentrations in primary melts from supra-subduction zones and mid-ocean ridges: Implications for H_2O storage and recycling in the mantle. *Earth Planet. Sci. Lett.* **137**(1–4), 45–55.

Straub, S. M., and Layne, G. D. (2003) Decoupling of fluids and fluid-mobile elements during shallow subduction: evidence from halogen-rich andesite melt inclusions from the Izu arc volcanic front. *Geochem. Geophys. Geosys.* **4**, ISI:000184337300001.

Stroncik N. A., and Haase K. M. (2004) Chlorine in oceanic intraplate basalts: Constraints on mantle sources and recycling processes. *Geology* **32**(11), 945–948.

Sun S. S., and McDonough W. F. (1989) Chemical and isotopic systematics of oceanic basalts; implications for mantle composition and processes. In *Magmatism in The Ocean Basins*., vol. 42, (eds. A.D. Saunders and M.J. Norry), pp. 313–345. Geological Society of London.

Sun W., Bennett V. C., Eggins S. M., Arculus R. J., and Perfit M. (2003a) Rhenium systematics in submarine MORB and back-arc basin glasses: laser ablation ICP-MS results. *Chem. Geol.* **196**(1–4), 259–281.

Sun W. D., Arculus R. J., Bennett V. C., Eggins S. M., and Binns R. A. (2003b) Evidence for rhenium enrichment in the mantle wedge from submarine arc-like volcanic glasses (Papua New Guinea). *Geology* **31**(10), 845–848.

Sun W. D., Arculus R. J., Kamenetsky V. S., and Binns R. A. (2004a) Release of gold-bearing fluids in convergent margin magmas prompted by magnetite crystallization. *Nature* **431**(7011), 975–978.

Sun W. D., Bennett V. C., and Kamenetsky V. S. (2004b) The mechanism of re enrichment in arc magmas: evidence from Lau Basin basaltic glasses and primitive melt inclusions. *Earth Planet. Sci. Lett.* **222**(1), 101–114.

Symonds R. B., Rose W. I., Bluth G. J. S., and Gerlach T. M. (1994) Volcanic gas studies—methods, results, and applications. In *Volatiles in Magmas.* , vol. 30, pp. 1–66. Mineralogical Society of America.

Taylor B. (1995) *Backarc Basins: Tectonics and magmatism.* Plenum, New York, pp. 524.

Taylor B., and Martinez F. (2003) Back-arc basin basalt systematics. *Earth Planet. Sci. Lett.* **210**, 481–497.

Tenthorey E., and Hermann J. (2004) Composition of fluids during serpentinite breakdown in subduction zones: evidence for limited boron mobility. *Geology* **32**(10), 865–868.

Wallace P. J. (2005) Volatiles in subduction zone magmas: concentrations and fluxes based on melt inclusion and volcanic gas data. *J. Volcanol. Geotherm. Res.* **140**(1–3), 217–240.

Webster J. D. (2004) The exsolution of magmatic hydrosaline chloride liquids. *Chem. Geol.* **210**(1-4), 33–48.

Webster J. D., Kinzler R. J., and Mathez E. A. (1999) Chloride and water solubility in basalt and andesite melts and implications for magmatic degassing. *Geochim. Cosmochim. Acta* **63**(5), 729–738.

Woodhead J. D., and Brauns M. (2004) Current limitations to the understanding of Re–Os behaviour in subduction systems, with an example from New Britain. *Earth Planet. Sci. Lett.* **221**(1–4), 309–323.

Woodhead J. D., Eggins S. M., and Johnson R. W. (1998) Magma genesis in the New Britain island arc; further insights into the melting and mass transfer processes. *J. Petrol.* **39**(9), 1641–1668.

Woodhead J. D., and Johnson R. W. (1993) Isotopic and trace-element profiles across the New Britain island arc, Papua New Guinea. *Contrib. Mineral. Petrol.* **113**, 479–491.

Wysoczanski R., and Tani K. (2006) Spectroscopic FTIR imaging of water species in silicic volcanic glasses and melt inclusions: an example from the Izu-Bonin arc. *J. Volcanol. Geotherm. Res.* **156**(3–4), 302–314.

Xiao Y. L., Hoefs J., and Kronz A. (2005) Compositionally zoned Cl-rich amphiboles from North Dabie Shan, China: Monitor of high-pressure metamorphic fluid/rock interaction processes. *Lithos* **81**(1–4), 279–295.

Xiao Y. L., Hoefs J., van den Kerkhof A. M., Fiebig J., and Zheng Y. F. (2000) Fluid history of UHP metamorphism in Dabie

Shan, China: a fluid inclusion and oxygen isotope study on the coesite-bearing eclogite from Bixiling. *Contrib. Mineral. Petrol.* **139**(1), 1–16.

Xiao Y. L., Hoefs J., Van den Kerkhof A. M., Simon K., Fiebig J., and Zheng Y. F. (2002) Fluid evolution during HP and UHP metamorphism in Dabie Shan, China: constraints from mineral chemistry, fluid inclusions and stable isotopes. *J. Petrol.* **43**(8), 1505–1527.

Xiao Z. F., Gammons C. H., and Williams-Jones A. E. (1998) Experimental study of copper(I) chloride complexing in hydrothermal solutions at 40 to 300 °C and saturated water vapor pressure. *Geochim. Cosmochim. Acta* **62**(17), 2949–2964.

Xiong X. L., Adam J., and Green T. H. (2005) Rutile stability and rutile/melt HFSE partitioning during partial melting of hydrous basalt: implications for TTG genesis. *Chem. Geol.* **218**(3–4), 339–359.

Yang K. H., and Scott S. D. (1996) Possible contribution of a metal-rich magmatic fluid to a sea-floor hydrothermal system. *Nature* **383**(6599), 420–423.

Yang K. H., and Scott S. D. (2002) Magmatic degassing of volatiles and ore metals into a hydrothermal system on the modern sea floor of the eastern Manus back-arc basin, western Pacific. *Econ. Geol.* **97**(5), 1079–1100.

Associate editor: Alan D. Brandon