First volatile inventory for Gorely volcano, Kamchatka

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[1] We report here the very first assessment of volatile flux emissions from Gorely, an actively degassing volcano in Kamchatka. Using a variety of in situ and remote sensing techniques, we determined the bulk plume concentrations of major volatiles (H_2O ~93.5%, CO_2, ~2.6%, SO_2 ~2.2%, HCl 1.1%, HF 0.3%, H_2 0.2%) and trace-halogens (Br, I), therefore estimating a total gas release of ~11,000 tons·day^{-1} during September 2011, at which time the target was non-eruptively degassing at ~900°C. Gorely is a typical arc emitter, contributing 0.3% and 1.6% of the total global fluxes from arc volcanism for CO_2 and HCl, respectively. We show that Gorely's volcanic gas (H_2O/SO_2 ~43, CO_2/SO_2 ~1.2, HCl/SO_2 ~0.5) is a representative mean end-member for arc magmatism in the north-west Pacific region. On this basis we derive new constraints for the abundances and origins of volatiles in the subduction-modified mantle source which feeds magmatism in Kamchatka. **Citation:** Aiuppa, A., G. Giudice, M. Liuzzo, G. Tamburello, P. Allard, S. Calabrese, I. Chaplygin, A. J. S. McGonigle, and Y. Taran (2012), First volatile inventory for Gorely volcano, Kamchatka, *Geophys. Res. Lett.*, *39*, L06307, doi:10.1029/2012GL051177.

1. Introduction

[2] Arc volcanism at convergent plate margins is the primary pathway for exchanges of volatile matter between the Earth's mantle and surface environments (e.g., the hydrosphere and atmosphere) [*Hilton et al.*, 2002]. The need to better understand the mechanisms and rates of volatile supply to the mantle via subduction, and volatile recycling through arc volcanism has motivated extensive work on the petrology of arc magmas [e.g., *Pearce and Peate*, 1995] and subducted sediments [*Plank and Langmuir*, 1998], and on the chemical and isotopic composition of volcanic gases in arc settings [*Fischer*, 2008]. The Kamchatka (K) peninsula, in the north-west of the Pacific 'Ring of Fire', is one of the most active volcanic arcs on Earth, with 29 historically erupting volcanoes along the ~700 km-long Eastern Volcanic Belt (EVB; Figure 1a). This runs parallel to the Kurile-Kamchatka (KK) trench where 80–100 My old oceanic Pacific plate is subducted underneath Eurasia at ~7.6–7.8 cm·year^{-1} [*Gorbatov et al.*, 1997]. Magma generation beneath Kamchatka arises from 5–18% partial melting of a subduction-modified DMM-like (Depleted MORB Mantle) source [*Portnyagin et al.*, 2007].

[3] Whilst volatile input and output fluxes are now reasonably constrained for some volcanic arcs, very little previous work has been devoted to the Kamchatkan case [*Taran*, 2009]. In particular, SO_2 flux data exist for only four of the ten persistently degassing volcanoes in the arc. *Taran* [2009] therefore outlined the need to considerably extend the study of gas compositions and fluxes from Kamchatka volcanoes in order to quantitatively assess their contribution to global volcanic emissions.

[4] The 11th field Workshop of the IAVCEI (International Association of Volcanology and Chemistry of the Earth's Interior) Commission on the Chemistry of Volcanic Gases (CCVG), held in Kamchatka in September 2011, provided us an apposite opportunity to perform such measurements, in particular, at Gorely volcano, located ~70 km south of Petropavlovsk-Kamchatsky (Figure 1a). Here we report on the very first compositional and volatile flux data for open-vent emissions from this very active volcano, obtained from combined in situ and remote sensing measurements. These results add to our existing knowledge of volcanic degassing in Kamchatka, and enhance constraints on the abundances and origins of volatiles from the mantle source which feeds volcanism in the north-west Pacific region.

2. Gorely Volcano

[5] Gorely is a large (25 km^3; 1830 m high) shield-like Holocene volcano located at the northern end of the southern segment of the EVB. It stands ~120 km above the slab surface and occupies a rear-arc position relative to the volcanic front (~15 km westward of the EVB [see *Duggen et al.*, 2007]). Gorely's active edifice has the form of a ~3 km linear ridge (oriented WNW), composed of at least three main coalescing volcanic cones (Gorely 1–3) that are hosted in a 30–40 ka old caldera [*Selyangin and Ponomareva*, 1999]. This caldera was formed during a large (~100 km^3) ignimbrite-forming andesite-dacite eruption. The post-caldera Holocene activity of Gorely 1–3 alternated between phases of persistent degassing and Vulcanian-style explosive eruptions, with periods of voluminous (>0.1 km^3) lava flow eruptions from the volcano's rift systems (Figure 1b) [*Selyangin and Ponomareva*, 1999]. All eruptions in the 20th century (1929–31; 1959–61; 1980–81; 1984–86) arose from the south-westernmost crater (500–700 m across) within the Gorely 2 cone, and were moderately explosive (VEI < 3) with emission of basaltic-andesitic ash. After the 1984–86 eruption, an acidic lake was formed in this crater, which has also manifested persistent fumarolic activity with steam plumes rising several km high on occasion (KVERT). At the time of our campaign, on September 6th 2011, vigorous jet-like degassing was taking place from a hot (~900°C) 34×45 m^2 open-vent (Figure 1c) and hot fractures in the northern wall of

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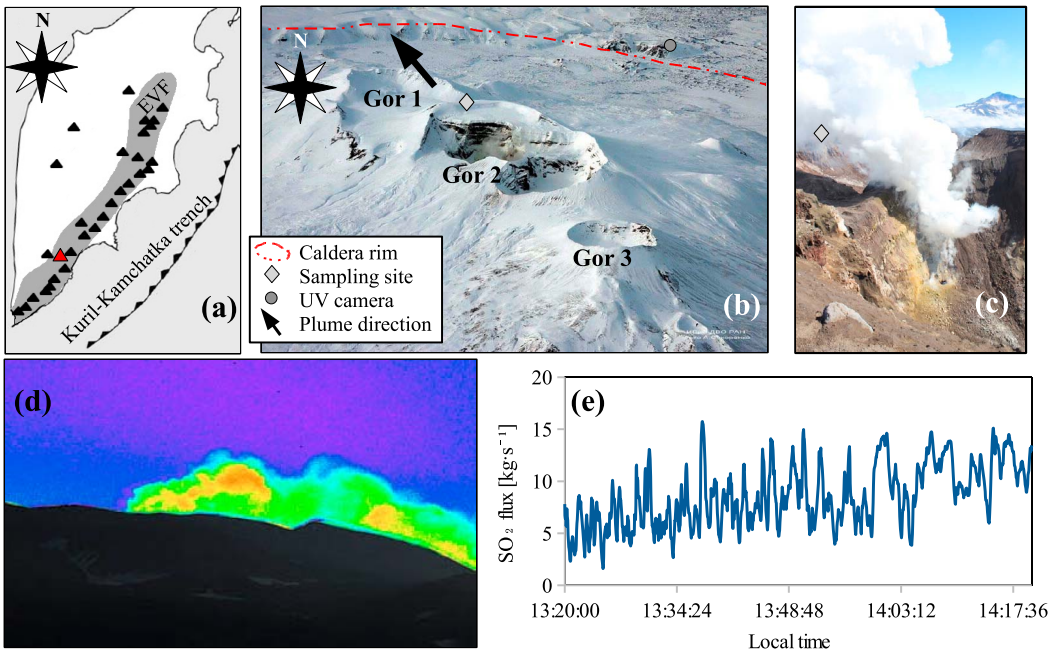

Figure 1. (a) Location of Gorely volcano (red triangle) and the Eastern Volcanic Front (EVF) (b) photo of Gorely summit (by A. Sokurenko; from KVERT web site) with location of observation sites; (c) the open-vent on September 6th (the diamond shows the MultiGAS site); (d) pseudo-colour image of SO_2 concentrations in the plume, derived from the UV camera; (e) ~1 h time-series of the SO_2 flux.

the crater. This open-vent degassing, which started in 2009 and has intensified since June 2010 (opening of a red glowing vent was first reported on June 16, 2010), was observed to display cyclical variations in magnitude and character (alternating between transparent blue venting and whiter vapour-richer fuming) over timescales of a few minutes.

3. Measurements

[6] A dual-UV camera set up (see auxiliary material for details) was used to obtain time series of the SO_2 flux released by Gorely, at a resolution of 0.33 Hz.[1] More than 5 hours of observations were performed from a site ~5 km north-east of the volcano's summit (Figure 1b). SO_2 fluxes varied considerably during our observations (from 2.6 to 16 $kg{\cdot}s^{-1}$) and showed periodic variations (pulsations of 150–400 s; Figure 1e), in tandem with the pulsed degassing behaviour evident at the summit vent. The mean SO_2 flux discharge over the measurement period was 800 ± 250 $tons{\cdot}day^{-1}$.

[7] We contemporaneously deployed a portable MultiGAS sensor [*Aiuppa et al.*, 2010] on the northern rim of Gorely crater, 300 m downwind of the source (Figure 1b), for measuring (at 0.5 Hz and for ~2 hours) the concentrations of major volcanogenic gas species in the plume. Due to the wind conditions the volcanic plume was often lofted gently above the instrument site, enabling good characterisation of the ambient air background. These concentrations obtained for H_2O (~11,0000 ppmV), CO_2 (~389 ppmV), SO_2 (<0.05 ppmV) and H_2 (~0.55 ppmV) are typical of *normal* air, as further confirmed by additional background measurements taken on the volcano's slopes. Intermittently, increased wind speed advected the plume to our instrument, leading to significant concentration increases in H_2O, CO_2, SO_2 and H_2 (by up to ~300, 8.4, 6.5 and 0.5 ppmV, respectively) with respect to ambient air. The positive correlations between background-corrected gas concentrations (Figure 2) demonstrate the strong volcanogenic signal. From the slopes of the best-fit regression lines, we derive the following characteristic molar ratios in the volcanic plume: H_2O/SO_2 (43 ± 13), CO_2/SO_2 (1.2 ± 0.1) and H_2/SO_2 (0.11 ± 0.02). H_2S was not detected throughout our measurements (H_2S/SO_2 <0.02) (see Table S1 in the auxiliary material).

[8] Sets of base-treated filter packs were simultaneously collected to derive the in-plume halogen (HCl, HF, Br and I) concentrations and the halogens/SO_2 ratios (Table S1). We find that Gorely's plume emissions display halogen/SO_2 and inter-halogen volatile ratios that are typical of arc volcanic gases [*Fischer*, 2008; *Aiuppa*, 2009]. This applies in particular to HBr/SO_2 and HI/SO_2 ratios ($5.3{\cdot}10^{-4}$ and $9.1{\cdot}10^{-5}$), even though available data for Br and I in arc volcanic gases are far less abundant than those for Cl and F. Moreover, our filter pack-based SO_2/HCl molar ratios of 1.8–2 fall well within the S/Cl range (1.2–2.7) for Kamchatka parental melts, as inferred from dissolved S and Cl in crystal-hosted melt inclusions [*Portnyagin et al.*, 2007]. In contrast, our Cl/F ratios (3.6–3.8) are at the upper limit for K parental melts (1.2–3.7 [*Portnyagin et al.*, 2007]), in view of the weaker degassing release of fluorine, which is rather more soluble than Cl in mafic magmas [e.g., *Aiuppa*, 2009].

4. Discussion

4.1. Gorely Gas Composition

[9] The molar composition of Gorely's magmatic gas is computed (Table S1) from the above volatile ratios, on the

[1]Auxiliary materials are available in the HTML. doi:10.1029/2012GL051177.

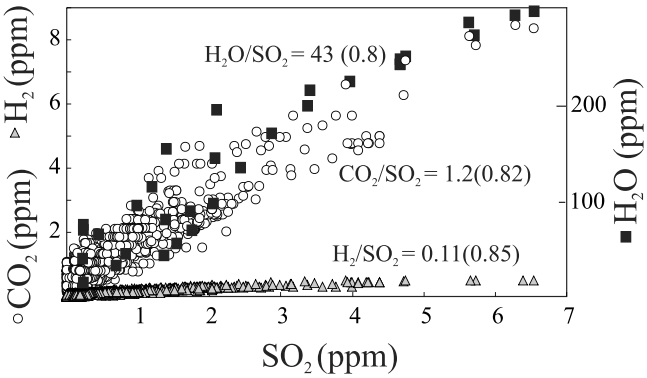

Figure 2. Scatter plots of major volcanic gas species in the plume (from MultiGAS). The derived X/SO_2 ratios are indicated (R^2 of regression line in parenthesis). SO_2, in the *x*-axis, is taken as a "plume marker" because of its very low atmospheric concentrations. Only in a few conditions (dense plume) was the *volcanic* H_2O signal distinguished over the large and fluctuating background.

basis that we measured all the significant components of high temperature volcanic gases except carbon monoxide. When compared with currently available data for high-T volcanic gases in the Kamchatka-Kurile arcs [*Fischer*, 2008], Gorely's gas is the poorest in water (93.5%), the richest in both CO_2 (2.6%) and SO_2 (2.2%), and moderately rich in HCl (1.1%). The H_2O content and H_2O/SO_2 ratio (43 ± 13) are even lower than those of 950 °C gases from Kudryavy volcano in the Kuriles [*Taran et al.*, 1995], the most accessible location for magmatic degassing in the entire arc (H_2O = 94.4–95.3% and H_2O/SO_2 = 46.5–52.5). Our results therefore contradict the previous suggestion [*Fischer*, 2008] of an exceptionally high H_2O/SO_2 (>250) *average* signature for Kamchatka's volcanic gases, which was probably biased by unusually SO_2-poor (<0.2%) samples from late-stage (S-depleted) lava flow degassing at Alaid, Kliuchevskoi and Tolbachik volcanoes (ten times poorer in SO_2 than central degassing from both Gorely and Kudryavy; both ∼2.0%). Our MultiGAS derived composition for Gorely is well matched with volcanic gas data from other basaltic arc volcanoes (e.g., Masaya, Villarrica, Miyakejima; H_2O: 94–95%) [*Shinohara*, 2008].

4.2. Volatile Budget

[10] The SO_2 flux of 800 ± 250 tons·day^{-1} we measured at Gorely on September 6th 2011 is the first ever reported for this volcano and the greatest yet determined for any volcano in Kamchatka [*Taran*, 2009]. Although we cannot evaluate the temporal stability of this rather large SO_2 release, this degassing rate from Gorely corresponds to a significant fraction (up to 40%) of the current estimated total from the entire K arc segment (≥2000 t·day^{-1} [*Taran*, 2009]) and exceeds the total estimated flux from the Kamchatka arc of ∼290 t/day, which was based on global extrapolations [*Fischer*, 2008]. The measured SO_2 flux, combined with the plume composition, allows us to assess Gorely's emission rates for all detected gas species (Table S1). The calculated fluxes range from 9700 tons·day^{-1} for H_2O to 0.14 tons·day^{-1} for HI, summing up to 11,000 tons·day^{-1} overall. These emission rates render Gorely as a typical arc emitter, contributing to about 0.6% (H_2O), 0.3% (CO_2), and 1.5–1.6% (SO_2, HCl) of the global volatile fluxes currently estimated for arc volcanism [*Wallace*, 2005; *Fischer*, 2008; *Taran*, 2009].

4.3. Gorely's Gas, an End-Member for the North-West Pacific Arc Region

[11] Our measurements are put in the context of previous Kamchatka gas observations in Figure 3. The diagrams illustrate the strong temperature dependence of measured gas compositions: low temperature (<300°C) volcanic gases, which are more affected by secondary processes (e.g., reactions with fumarolic wall rocks, condensation of sublimates/incrustations and liquid water-gas interactions) show a wide compositional range, typically with high CO_2/SO_2 and SO_2/HCl ratios (due to losses of SO_2 and the even more soluble HCl); whereas high-temperature (>445°C; the boiling point of native sulphur) gases are far less affected by such processes, displaying lower values of CO_2/SO_2 and SO_2/HCl, in a narrower range. Hence, a meaningful comparison between different arcs is possible only for high-temperature volcanic gas samples. As previously mentioned, our Gorely data closely match the compositions of high-T (>900°C) magmatic gases from Kudryavy [*Taran et al.*, 1995; *Fischer et al.*, 1998], suggesting a magmatic signature with CO_2/SO_2 = 1–1.4 and SO_2/HCl = 1.9–3 for the Kamchatka-Kurile (KK) arc system.

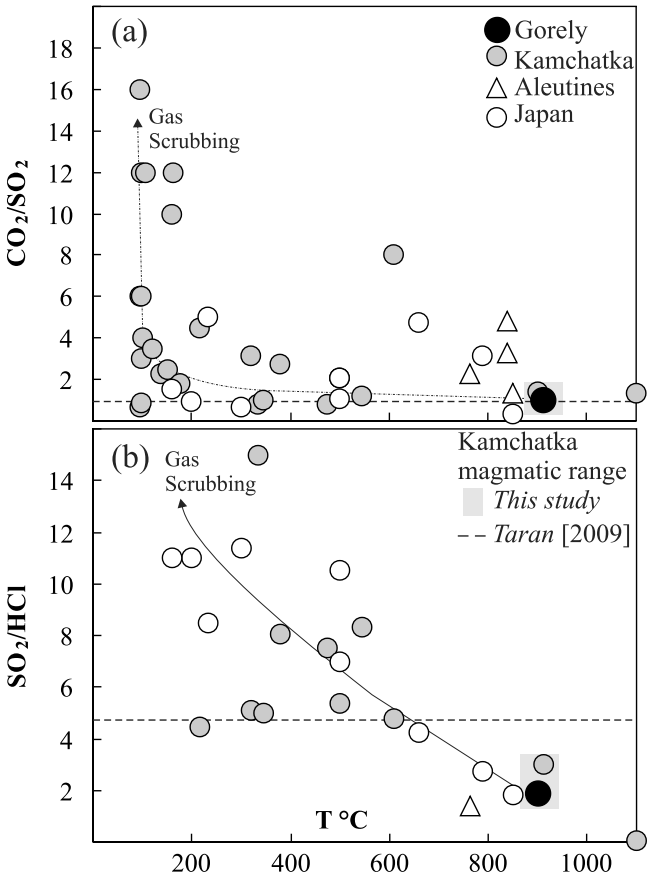

Figure 3. Temperature dependence of (a) CO_2/SO_2 and (b) SO_2/HCl molar ratios in volcanic gas samples from the NW Pacific. Data from *Fischer* [2008], *Shinohara et al.* [2008], *Taran* [2009] and *Werner et al.* [2011, and references therein].

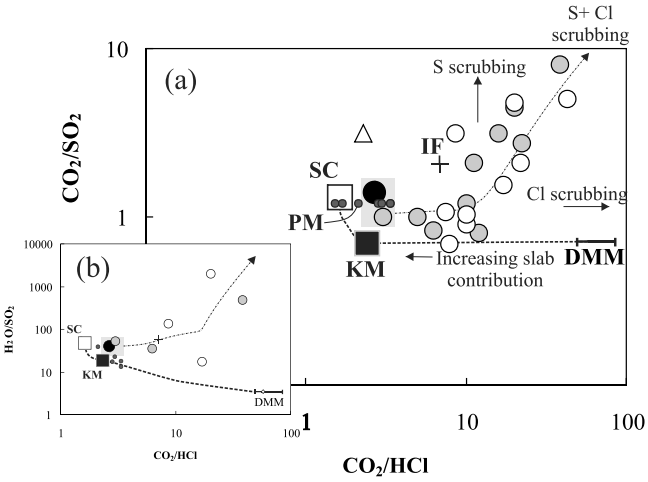

Figure 4. Volatile ratios in Gorely's gas plume compared with gas data across the NW Pacific (source and symbols as in Figure 3). The compositional fields of Kamchatkan parental melts (PM) [*Portnyagin et al.*, 2007], DMM [*Saal et al.*, 2002], subducted materials entering the slab (input fluxes, IF [*Taran*, 2009]), and our inferred compositions for the Kamchatkan source mantle (KM) and the slab-derived fluid component (SC), are also shown. See text for discussion.

[12] Figure 3 additionally shows that gas data from Japanese and Alaskan volcanoes plot on the same temperature-composition array as the KK volcanic gases. High-temperature (≥700°C) volcanic gases from Japan clearly converge onto low CO_2/SO_2 (0.4–3) and SO_2/HCl (1.8–2.8) ratios, similar to those of Gorely and the KK arc. Measurements at poorly accessible Alaskan volcanoes have been more sporadic, in comparison, (see *Werner et al.* [2011] for a recent review), and since the majority of these volcanoes are glaciated the possibility of gas scrubbing merits attention. However, *Werner et al.* [2011] argued that during recent (1980s to present) volcanic unrests at six Alaskan (Cook Inlet) volcanoes, the gas compositions typically converged toward a relatively narrow CO_2/SO_2 ratio range of 0.5–2, indicating truly magmatic conditions with little or no sulphur scrubbing. Indeed, our Gorely gas composition plots in the very middle of this range (Figure 3). In comparison, the mean CO_2/SO_2 ratios (1.4–4.8; Figure 3a) of high-temperature gases and/or eruptive plumes released during (or shortly after) magmatic eruptions at Augustine (1976, 1989, and 2006) and Redoubt (1989–90 and 2009) volcanoes in Alaska fall at or even above the upper limit of the above range, which may indicate short-lived supply of deeper-derived (CO_2-enriched) magmatic vapour during paroxysmal eruptive phases.

[13] In summary, from this regional comparison we find that high temperature volcanic gases from the Kamchatka-Kurile, Japan and Alaska arcs converge into a narrow compositional range (Figure 3), even though they are separated by thousands of kilometres. Such an observation suggests relatively uniform abundances and behaviour of volatiles in the corresponding magma sources. In that respect, we note that Gorely's gas composition, especially its low H_2O/SO_2 (43), fits remarkably well with the volatile abundances and average H_2O/S (39) ratio measured in feeding EVB parental magmas [*Portnyagin et al.*, 2007]. Taking into account the arguments above, we therefore propose that Gorely's gas composition may represent a good proxy for the magmatic gas end-member composition in the north-west Pacific region, as depicted in Figure 4 and discussed below.

5. Concluding Remarks: Insights Into Volatile Contents and Origins in Kamchatka Mantle

[14] Accepting that Gorely's gas plume composition carries a strictly magmatic volatile signature, as argued above, our results provide new constraints on both the CO_2 abundance and the origins of volatile components in the Kamchatka mantle source. The H_2O, S, Cl and F contents of K parental magmas have recently been quantified by *Portnyagin et al.* [2007]. By combining their parental melt S content (0.07–0.27%) with our inferred CO_2/SO_2 ratio (1.2) in Gorely's volcanic gas, a CO_2 content of 0.13–0.45% in these parental melts is inferred. This is in the range estimated for most arc magmas [*Fischer and Marty*, 2005; *Wallace*, 2005]. Following the procedure of *Duggen et al.* [2007], the CO_2-completed volatile content of Kamchatka parental melts (Figure 4) can then be used to calculate the volatile composition of the K mantle source. We did just this by solving a batch melting equation for each volatile, assuming a 10% mantle melting fraction [*Duggen et al.*, 2007] and using vapour-melt distribution coefficients from *Saal et al.* [2002]. The so-calculated volatile ratios in the K mantle (KM) are clearly distinct from DMM (data from *Saal et al.* [2002]), pointing to pervasive mantle fertilization by slab-derived fluids (Figure 4). Furthermore, on the basis that KM involves 0.3–1 wt% addition of a slab component (SC) to DMM [*Duggen et al.*, 2007] and, using simple mass balance equations, we compute a SC bulk fluid molar composition of ∼87% H_2O, ∼5.8% CO_2, ∼3.2% S, ∼2.9% Cl and ∼0.4% F (Figure 4). Since major silicate components are not included in the calculations, our inferred SC volatile contents are maxima, whilst the chemical ratios should be close to the actual values. According to mass balance calculations, the SC would contribute 94–98% of total H_2O and Cl, ∼70% of the CO_2, and 38–41% of total S and F in generated magmas. Our estimated SC composition diverges from the average volatile composition of subducted materials entering the slab - the K arc input fluxes (IF) - hypothesised by *Taran* [2009] (Figure 4). We stress, however, that the latter estimate is based upon compositions of sediments and altered ocean crust for Pacific arc segments other than Kamchatka (for which such data, unfortunately, are unavailable): this may explain, at least partly, the mismatch between SC and IF found here. In particular, the carbon-poorer signature of our SC relative to *Taran*'s [2009] IF, in accord with the low CO_2/SO_2 signature of the KK gases, could be explained by the relative absence of subducted carbonate sediments in the NW Pacific, in comparison to other arc segments [*Plank and Langmuir*, 1998]. Alternatively, less effective carbon extraction from subducted materials (with respect to the more easily released Cl), and/or carbon-rich sediment accretion/off-scraping [*Hilton et al.*, 2002] might contribute to this discrepancy. Further studies will be needed to resolve this issue.

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