An alternative approach using integrated gamma-ray and geochemical data to estimate the inputs to subduction zones from ODP Leg 185, Site 801

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[1] The goal of the subduction factory project is to obtain a better understanding of processes occurring at convergent margins and performs mass balance calculations for tracer elements. As part of this project, a major objective of ODP Leg 185 is to determine the chemical composition of the inputs to the West Pacific Subduction Factory for use in calculations of elemental mass balance across the subduction zone. To understand such elemental budgets, it is critical to know the lithological diversity and chemical characteristics of the down going oceanic plate. Hole 801C, located ocean-ward of the Mariana island arc system, is the most complete section of old oceanic crust sampled to date but, core recovery in basement holes is often poor (e.g., <30%) resulting in a bias such that the less altered material is preferentially recovered. Integration of drilled cores and downhole wire line logging data was performed to reconstruct a complete section of the drilled basement. Furthermore we integrate gamma ray logging data with the geochemical analyses of recovered cores to estimate the average composition, in terms of potassium and uranium, of the volcanic section in Hole 801C. We used FMS (Formation MicroScanner) images to relocate the samples with respect to the logging depth and to directly compare the logging data and the geochemical data. We demonstrate that the logging tool is well calibrated for K and U in the basement and that differences observed between K₂O and U contents measured by the tool and by geochemistry are strongly dependent on the nature of the samples. The average K₂O concentration of Hole 801C basement section is 0.34 wt.% using core-derived proportions, 0.51 wt.% using log-derived proportions and 0.47 wt.% using the gamma ray data. In the same manner the average U concentrations are respectively 0.34 ppm, 0.39 ppm and 0.42–0.5 ppm. This implies that K and U budgets recycled in the Mariana subduction zone are 20–50% higher than previously reported. These results demonstrate that a careful core-log-geochemical integration is essential to accurately estimate the composition of a drilled section and in order to better constraint chemical fluxes into subduction zones.

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Theme: Oceanic Inputs to the Subduction Factory

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1. Introduction

[2] The Subduction Factory project aims to perform mass balance calculations for tracer elements, and measures the chemical fractionation occurring between elements by comparing the inputs, at trenches, and the outputs at the arcs, of subduction zones [Morris *et al.*, 1998; Plank *et al.*, 1998]. This goal requires reliable, quantitative and representative, input and output data in terms of both compositions and volumes.

[3] Ancient Pacific crust (Jurassic, [Pringle, 1992; Bartolini and Larson, 2001]) about to be subducted at the Mariana-Izu-Bonin subduction zone was drilled during ODP Legs 129 and 185 to sample the material soon to be subducted. Several sites (including 801 and 1149) were drilled and logged seaward of the Mariana and Izu-Bonin trench systems (Figure 1). The processes operating within the arc systems and the physical attributes of the subduction zones have been extensively characterized such that the subduction geometry [Taylor, 1992; Van der Hilst and Senon, 1993; Fryer *et al.*, 1999], the convergence vectors, the thickness of upper plate and slab temperature, are all fairly well defined [Van der Hilst and Senon, 1993; Fouch and Fischer, 1996; Suyehiro *et al.*, 1996]. Complete sediment subduction occurs at both the Mariana and Izu-Bonin trenches [Taylor, 1992]. The upper plate in both cases is oceanic, so the effects of crustal contamination on arc magmas are minimal. However, there are variations in the geochemical signal of the arc volcanoes both along strike and across the Mariana-Izu-Bonin volcanic arc system [Stern *et al.*, 1990; Tatsumi *et al.*, 1992; Elliot *et al.*, 1997; Peate and Pearce,

1998; Ishikawa and Tera, 1999]. These variations may be attributed to a number of factors, such as the nature of the inputs to the subduction zone, the processes operating within the subduction zone, the physical attributes of the subduction zone, or a combination of any or all of these. There are a wide range of inputs to the system including sediments, seamounts and altered oceanic crust. Key tracer elements for mass balance calculations, such as Th, Rare Earth Element (REE), Ba or Be are stored within sediments deposited on the subducting plate but the principal reservoir for other elements, particularly K, B, U, CO₂ and H₂O, is the uppermost, oxidised portion of the volcanic ocean basement. The input of these elements to an arc system varies as a function of both the sediment composition [Plank and Langmuir, 1998] and the structure of the volcanic basement [Staudigel *et al.*, 1995, 1996; Alt *et al.*, 1998; Alt and Teagle, 1999]. It is therefore critical to obtain accurate estimates of the composition of the subducted oceanic crust.

[4] A major problem arising during drilling in ocean crust is that complete core recovery is rare due to the fractured nature of the rocks and large contrasts in the competency of the material drilled. It is therefore difficult to determine a reliable and representative average composition for the oceanic crust, particularly considering that the altered or brecciated portions, containing most of the mobile elements, are usually more poorly recovered [Brewer *et al.*, 1998; Lovell *et al.*, 1998; Brewer *et al.*, 1999]. During ODP Legs 129 and 185, 474 m of oceanic crust was drilled at Hole 801C, thus providing a significant penetration of the upper oceanic basement, but only 47% of the basement cored was recovered (Figure 2).

Figure 1. Location map of ODP Leg 185 Sites 801 and 1149 in relation to the Mariana arc system.

[5] To estimate the overall composition of the oceanic crust, one approach utilises a physical mixture of different rock types, with sample powders combined to produce a “composite” sample [Staudigel *et al.*, 1995, 1996; Plank *et al.*, 2000]. Small amounts of material from a large number of samples are combined in one or several composite samples. However, even if the recovered cores are quantitatively described, it is difficult to combine each rock type in the correct proportions because the cores are generally not fully representative of the drilled basement.

[6] In this paper, we present an alternative approach, in which geochemical analyses and logging data, specifically the gamma-ray data are integrated to provide a continuous record of geochemical variations. We also demonstrate that gamma ray data,

yielded by wire line logging, can be used as a proxy for K_2O and U contents downhole.

2. Geological Background, and Results From Core-Log Integration

[7] Hole 801C is located within the Pigafetta Basin in West Pacific oceanic crust (Figure 1). It lies within the Jurassic magnetic quiet zone and penetrates the oldest oceanic crust drilled to date, at 166 ± 4.5 Ma from radiometric dating [Pringle, 1992] or 170–175 Ma from biostratigraphic studies [Bartolini and Larson, 2001]. This crust formed at fast spreading rates [Plank *et al.*, 2000]. Hole 801C was first drilled during ODP Leg 129, to a total depth of 594 meters below seafloor (mbsf) [Lancelot *et al.*, 1990]. The entire sedimentary pile was drilled dur-

Figure 2. Results of the core-log integration study. Shown from left to right are the recovery during leg 185, the lithology column established from the cores, the basement section units and the lithology column extracted from the downhole logging data. Modified from *Barr et al.* [2002].

ing Leg 129 and approximately 130 m into the basement. During ODP Leg 185, the hole was re-entered and deepened to 935.4 mbsf [Plank *et al.*, 2000]. Site 801C was first logged during ODP Leg 144 [Shipboard Scientific Party, 1993; Haggerty *et al.*, 1995] and re-logged during Leg 185 [Plank *et al.*, 2000]. The basement stratigraphy of the logged interval in Hole 801C (Figure 2) comprises seven major eruptive sequences (see also Plank *et al.*

[2000] and Barr *et al.* [2002] for a more detailed description). The uppermost section consists of alkali basalts and extends from 490 to 510 mbsf [Floyd and Castillo, 1992]. A sequence of tholeiitic upper massive flows, from 530 to 590 mbsf, is separated from the alkali basalts by a first hydrothermal zone at 510–530 mbsf. The next section consists of pillows and flow units, down to 715 mbsf and a second hydrothermal zone occurs within this

sequence at around 625 mbsf. The lower sequence of massive flows extends down to 835 mbsf and is followed by a thick breccia unit (Figure 2).

[8] Wire line logging data, including physical properties measurements such as velocity, resistivity, porosity, density, gamma ray and FMS (Formation MicroScanner) images were used to reconstruct a complete basement section [Barr *et al.*, 2002]. The rock types were first identified within recovered cored intervals and criteria were defined to extrapolate to sections of poor recovery. This integration of core and logging data has allowed us to establish a continuous downhole stratigraphy. Results of this integration are summarized in Figure 2 (and presented in detail in Barr *et al.* [2002]). The results highlight a significant difference in the proportions of pillow basalts and breccia, with twice the amount of pillow material (32.7% compared with 15.3% present or 27.8% if recovered core proportions are expanded to 100% recovery), and six times more breccia (31.3% compared with 4.5% present or 8.1% for the expanded value) than is indicated by considering the recovered core description alone. The proportion of massive basalt is approximately the same for the two approaches (27.4% compared with 33.4% present) but highly overestimated if an expanded approach is adopted (60.6%) (see also Barr *et al.* [2002] for a complete discussion). Similarly the proportions of interpillow sediments and hydrothermal material are almost equal, although it should be noted that the proportion of interpillow sediment reported after core-log integration is likely an underestimate, because some pillow or breccia units contained sediments that were not distinguished as separate logging units [Barr *et al.*, 2002].

3. Analytical Techniques

3.1. Logging Data

[9] The natural radioactivity of the formation was measured using the Hostile Environment Natural Gamma Ray Sonde (HNGS) and the Natural Gamma Ray Tool (NGT). The HNGS and NGT record the radioactivity of a formation, which is due to the presence of the naturally occurring radioactive isotopes of K, U and Th [Rider, 1996]. Conventional tools consist of a scintillation counter,

normally a sodium iodide crystal, and a photomultiplier. Measured energy values can be used to identify the gamma radiations in several energy windows, which in turn can be used to separate the energy peaks of the individual radioactive elements [Rider, 1996]. Although the data for the different tool runs are all in good agreement, we have used the data from the main HNGS run from Leg 185 for this study. The HNGS makes similar measurements to the NGT but the HNGS has a greater sensitivity and is capable of making measurements in difficult hole conditions. The HNGS employs bismuth germanate scintillation detectors, which are more sensitive than the sodium iodide crystal used by the NGT and afford better nuclear decay statistics. The HNGS measures total gamma and uses 5-window spectroscopy to resolve the detected spectrum into K, U and Th concentrations. The high-energy part of the spectrum is divided into three energy windows, each covering a characteristic peak of the three radioactivity series. The concentration of each component is determined from the count rates in each window. Because the high-energy region contains only 10% of the total spectrum count rates, the measurements are subject to large statistical variations, even using a low logging speed. The results are considerably improved by including the contribution from the low-energy part of the spectrum. Filtering techniques are used to further reduce the statistical noise by comparing and averaging counts at a certain-depth with counts sampled just before and just after. The final outputs are the total gamma ray, a uranium-free gamma ray measurement, and the concentrations of potassium, thorium, and uranium. A real time borehole size correction is also applied to the data during acquisition. The concentrations of radioactive elements are generally very low in fresh Mid-Ocean Ridge Basalts (MORB), but the gamma ray log can be a good indicator of the extent of alteration degree as it is sensitive to the presence of potassium-bearing minerals and secondary minerals have relatively high K contents [Harvey *et al.*, 1998; Borehole Research Group, 2000].

[10] The sampling interval of the tool is 15 cm and its vertical resolution is estimated to 46 cm [Rider, 1996; Plank *et al.*, 2000]. The radius of investiga-

tion of the tool depends on several factors such as the hole size, the mud density and the energy of the gamma rays (a higher energy gamma ray can reach the detector from deeper in the formation) [Borehole Research Group, 2000]. The concentrations measured by the tool are representative of a specific volume and the signal of a small feature, a vein for example, is “diluted” by the signal of the surrounding basalt. K₂O, U and Th contents reported by the tool in a specific interval can therefore be different than those measured on specific samples, which usually sample a smaller volume.

[11] Together with gamma-ray data we used FMS images to help relocating the samples and to identify the un-recovered material. The FMS is a micro-electrical imaging device that responds to relative differences in conductivity in the borehole wall. The images can be regarded as oriented resistivity maps of textural variations in the borehole walls, reflecting resistivity contrasts and porosity and grain size variations between the various lithologies. Dark and light colors indicate low and high micro-resistivity respectively [Brewer *et al.*, 1998; Lovell *et al.*, 1998; Brewer *et al.*, 1999; Barr *et al.*, 2002].

3.2. Geochemical Data

[12] Several sets of data were used for this study. Whole rock chemical analyses from ODP leg 129 samples are reported in Lancelot *et al.* [1990] and Castillo *et al.* [1992]. The additional analyses from ODP leg 185 were performed on board by XRF [Plank *et al.*, 2000] and at Boston University by ICP-AES (major elements) and ICP-MS (trace elements) (K. A. Kelley *et al.*, The Composition of Altered Oceanic Crust at ODP Sites 801 and 1149, manuscript submitted to *Geochemistry, Geophysics, Geosystems*, 2002, hereinafter referred to as Kelley *et al.*, submitted manuscript, 2002). Additional information on analytical techniques and errors can be found in Kelley *et al.* (submitted manuscript, 2002).

3.3. Multi Sensor Track Natural Gamma Ray (MST-NGR) Data

[13] NGR emission was recorded for all core sections to measure variations in radioactive counts

of sample rocks during Leg 185 [Plank *et al.*, 2000]. The NGR system records radioactive decay of ⁴⁰K, ²³²Th, and ²³⁸U, three long-period isotopes that decay at an essentially constant rate within measurable timescales. NGR emission was measured every 10 cm for a 20-s period. The NGR instrument was calibrated with a thorium source and background counts measured using a core liner filled with distilled water averaged 11.75 cps over a 30-min measurement period. Measurements in counts per second can be qualitatively compared to the API (American Petroleum Industry) units obtained from borehole wire line logging. Calibration tests were undertaken during Leg 185 and are described in details in Plank *et al.* [2000]. These have allowed us to estimate K₂O concentrations (in wt.%) from the NGR data (in count per second) in order to compare them with the logging data. This calibration assumes that the MST-NGR variations are largely because of K variations and was defined for the tholeiitic section of Hole 801C basement. The MST-NGR data were therefore not used to calculate an average composition of the alkali upper section of the basement.

4. Results

4.1. Gamma Ray Data With Depth

[14] K₂O, U and Th contents, extracted from the gamma ray measurements (Figure 3) indicate a general decrease in radioactivity with depth, similar to the data collected during Leg 144 where the depth profiles overlap (483–560 mbsf) [Shipboard Scientific Party, 1993; Plank *et al.*, 2000]. Overall, there is a good match between the tool measurements and the geochemical analyses. K₂O contents are high (>2%) in the top 100 m of the basement, corresponding to the upper alkali lava sequence (Figure 2) [Lancelot *et al.*, 1990; Castillo *et al.*, 1992; Floyd and Castillo, 1992; Floyd *et al.*, 1992; Plank *et al.*, 2000]. There is good agreement in this section between the measured samples and the gamma ray data. In the lower section, concentrations shown by both types of data are much lower (<1% on average) but chemical analyses of some of the samples display higher contents (breccias, sediments and some pillow basalts).

Figure 3. Plots of K_2O (wt%), U (ppm) and Th (ppm) versus depth of gamma ray logging data and geochemical analyses of discrete samples.

The gamma ray curve does not show such high K concentrations but these brecciated or more altered intervals are, however, marked by peaks on the log curve.

[15] There is also a good agreement between the U content measured in the samples and the gamma ray logs. The overall concentrations are low, as expected for MORB (0.3 ppm on average [Staudigel *et al.*, 1996]). The difference in absolute concentration results in a more scattered curve for the gamma ray measurements. As noticed for K_2O , some samples display high U contents, probably reflecting a high degree of alteration and the presence of carbonate veins that are hosts for U [Farr *et al.*, 2001]. These intervals can be also picked up in the gamma ray curve.

[16] Th contents are high in the upper alkali lavas (~ 2.5 ppm) and decrease down section with lower Th concentrations (< 1 ppm). Within a section between 525–575 mbsf, there is a strong discrepancy

between the very low values measured in the samples, which are usual for MORB, and the higher values reported by the tool. The source of these high thorium values is not well understood and a similar pattern of thorium concentration is observed in the Leg 144 logging data [Shipboard Scientific Party, 1993]. This inconsistency probably reflects an artefact from the spectral processing of the HNGS and NGT tools and Th concentration are not used further in this study.

4.2. Methodology

4.2.1. Sample Location

[17] One problem arising with drilling in ocean crust is that the exact sample location is lost during the drilling process. On average, a 9.5 m interval is drilled for each core. When recovery is $< 100\%$, it is ODP curation convention that the entire core will be shifted up to the top of the core barrel. The overall relative stratigraphy of the section is therefore

Figure 4. Example of sample relocation on core 1R, section 1 and 2. As highlighted by arrows, specific features such as veins or interpillow intervals, identified on digital images of the recovered cores and the FMS images are used to relocate the core samples. This illustrates how the FMS images were used to assess the new depth of the samples. In this case, the logging data enable to relocate section 2 with respect to section 1 and show that nothing was lost in these intervals.

maintained but the depths of the different pieces are not their true depths. In contrast, the logging tool measurements give a continuous record downhole, with absolute depths below seafloor.

[18] In order to directly compare logging data and data measured on discrete samples it is critical to

relocate the samples relative to the logging depths. To do this, we have matched the FMS images with images of the recovered cores. Using specific features, such as thick veins or breccia in-intervals, on the FMS images we were able to relocate the samples within the 9.5 m interval drilled by that core (Figure 4). This allows the relocation of the

Figure 5. Plot of recovery (%) versus the error on the sample relocation (m). There is a clear correlation between these two parameters and the error on location increases when the recovery decreases.

different sections of the core and therefore enables us to attribute, within error, its true depth to each sample. The error on the relocation shows an inverse relationship with the recovery (Figure 5) but is also dependent on the number of identifiable features within the core, which can be used to match the core with the FMS image. For example, in a continuous interval of homogeneous massive basalts, there is limited variation within the FMS images or the rocks recovered. It is therefore difficult to accurately relocate a sample.

4.2.2. Direct Comparison of Logging Data and Geochemical Data

[19] Once the samples have been relocated with respect to the logging depths, the gamma ray data and the whole rock geochemical analysis for K_2O and U can be compared directly (Figures 6 and 7). On overall the correlations between the two data sets is good indicating that the gamma ray logging tool measurements are reliable. Some scatters is observed but can be related to various factors described in the section below. The common source of error for each lithology and chemical element is the error on the sample relocation as described in the previous section.

4.2.2.1. Massive Basalts

[20] Major elements (including K_2O) were analysed on 109 samples of massive basalt [Lancelot *et al.*, 1990; Castillo *et al.*, 1992; Plank *et al.*, 2000; Kelley *et al.*, submitted manuscript, 2002]. Alkali basalts (27 samples) can easily be distinguished from the tholeiitic basalts with their K_2O contents (1.2–6.4 wt.% and <1 wt.% respectively, Figure 6a). The agreement between the wire line logging and the analytical measurements for massive basalts is very good (note that the highest concentrations have the greatest scatter in Figure 6a) with most of the samples plotting on a one to one line (Figure 6a). Scatter observed within the alkali basalt, toward high values can be related to the degree of alteration of the individual rock sample. For the massive basalts with the lowest concentrations of K_2O (<0.5 wt.%, Figure 6e) the correlation is weaker and the values extracted from the logging tool tend to be higher than those from the chemical analyses. Errors on the gamma ray values are estimated to 10% for K_2O concentrations <1 wt.% and 5% for the chemical analyses (Figure 6e). However, the weaker correlation observed on Figure 6e indicates that these errors might be higher. This also illustrates a major difference between the two techniques. For the chemical analyses only small, very fresh samples were chosen and these yielded very low K_2O contents. On the other hand, the logging tool measures a larger volume, which may include more altered portions, therefore giving higher K_2O contents. Despite these differences between the two data sets this do not, in our opinion, rule out the method. In fact, K_2O concentrations in massive basalts are very low and their influence on the average composition calculated per core (see below) will be low. For example, using data reported in Table 1 (Core 12R) an increase of 100% K_2O on the average massive basalt composition (from 0.05 wt.% to 0.1 wt.%) will result only in a 10% difference in the average K_2O content for the core (from 0.29% to 0.32% using the core-derived proportions and from 0.79% to 0.83% using the log-derived proportions, Table 1).

[21] U was analysed on 36 massive basalt samples (9 alkali basalts and 25 tholeiites, Figure 7a) [Castillo *et al.*, 1992; Kelley *et al.*, submitted

Figure 6. Plots of K_2O (wt.%) measured on discrete samples versus K_2O (wt.%) measured by the gamma ray logging tool for the different rock types identified during Leg 185. (a) Massive basalts; (b) pillow basalts; (c) breccia; (d) sediments and hydrothermal units; (e) zoom of plots Figures 6a and 6b. Errors bars represent 5% error for the chemical analyses and 10% error for the gamma ray data.

manuscript, 2002]. As for K_2O , the alkali basalts are easily distinguished by higher U concentrations ($U > \sim 1$ ppm) and the tholeiites display low U contents ($U < \sim 0.5$ ppm) (Figure 7a). The correlation between the chemical analyses and the logging data is fairly good given that the detection limit of the tool is usually estimated to 1 ppm. The

gamma ray data tend to be higher than the chemical analyses, which might also be related to the averaging effect of the logging tool.

4.2.2.2. Pillows Basalts

[22] K_2O was measured on 90 samples of pillow basalt [Lancelot *et al.*, 1990; Castillo *et al.*, 1992;

Figure 7. Plots of U (ppm) measured on discrete samples versus U (ppm) measured by the gamma ray logging tool for the different rock types identified during Leg 185. (a) Massive basalts; (b) pillow basalts; (c) breccia; and (d) sediments and hydrothermal units.

Plank et al., 2000; Kelley et al., submitted manuscript, 2002]. The K_2O contents measured on discrete samples of pillow basalts cover a larger range than for massive basalts, from ~ 0.1 wt.% up to 7 wt.%. The agreement between the two datasets is fairly good for the low concentrations ($0 < K_2O < 1$ w%) (Figures 6b and 6e). For the highest concentrations, the K_2O contents measured on individual samples are higher than those reported by the

gamma ray tool (Figure 6b). For concentrations below 0.5 wt.%, the concentrations measured by the logging tool are higher than those obtained from the chemical analyses, as observed for the massive basalts (Figure 6e).

[23] U was analysed on 26 samples [*Castillo et al.*, 1992; Kelley et al., submitted manuscript, 2002] from the tholeiitic section. As observed for the

Table 1. Example of Calculation for Core 12R^a

Lithology	Core-derived proportions (%)	Proportions upscaled to 100%	Log-derived proportions (%)	K ₂ O content (%)	<i>n</i>
Breccia	1.6	3.1	25.6	2.44	2
Massive basalt	44	84.7	44	0.05	3
Pillow	4.2	8	28.2	0.25	6
Sediment	2.2	4.2	2.2	3.48	1
Total	52	100	100		
Non recovered	48				
K ₂ O average for core 12R (%)					
From core	0.29				
From logs	0.79				
Logging data	0.76				

^a *n* is the number of samples used.

massive basalts, the correlation between the two data sets is less well defined for U than for K (Figure 7b).

4.2.2.3. Breccia

[24] K₂O was measured on 21 samples of volcanic breccia [Lancelot *et al.*, 1990; Castillo *et al.*, 1992; Plank *et al.*, 2000; Kelley *et al.*, submitted manuscript, 2002]. As observed for pillow basalts, K₂O concentrations measured on discrete samples display a large range (~0.1–>4 wt%) and are higher than those reported by the logging tool (Figure 6c). There is, however, a close correlation between the nature of the samples and the difference between the two data sets. Samples, which show the highest K₂O concentrations in the chemical analyses, are also those that contain more matrix than basalt clasts (see also discussion and Plank *et al.* [2000] for a full description of the samples).

[25] U was analysed on 16 samples from the tholeiitic section [Castillo *et al.*, 1992; Kelley *et al.*, submitted manuscript, 2002]. The correlation between the two data sets is fairly good as most samples plot close to the one to one line (Figure 7c).

4.2.2.4. Sediments and Hydrothermal Units

[26] K₂O was measured on 10 samples of inter-pillow sedimentary material and 4 samples from both upper and lower hydrothermal units [Lancelot *et al.*, 1990; Plank *et al.*, 2000; Kelley *et al.*, submitted manuscript, 2002]. The sediments samples display similar trends to those observed for pillow basalts and breccia. K₂O contents range

from ~0.1 wt.% to ~4 wt.% and K₂O contents calculated from the logging tool data are lower than those measured on discrete samples (Figure 6d). All the samples from the hydrothermal units plot within a narrow range and both techniques yielded very low K₂O contents (<0.1 wt.% for the chemical analyses and <0.5 wt.% for the gamma ray tool) (Figure 6d). Given the very small number of samples, it is difficult to give a reliable interpretation on the hydrothermal units.

[27] U was analysed on 7 sediment samples and 2 hydrothermal samples [Kelley *et al.*, submitted manuscript, 2002]. Given the low U contents of these samples, the correlation between the two data sets is reasonably good for both the sediments and the hydrothermal units (Figure 7d).

4.2.3. Average K₂O and U Contents Per Core

[28] To estimate the K₂O and U budgets in Hole 801C basement, average contents were calculated for each core using the expanded core-derived proportions, the log-derived proportions and the gamma ray logging data. For each core an average composition is obtained by a mass balance calculation. K₂O contents calculations for core 12R are reported in Table 1 and Figure 8 as an example. The average chemical composition of samples from each lithology (Table 1) is first balanced by the proportions of each lithology recovered in the core and scaled to 100% recovery (Figure 8, Table 1). Then, using the core-log integration results, a rock type is attributed to the un-recovered interval and

Figure 8. Example (core 12R) of K_2O average content calculation per core. The core lithology, the FMS images, the gamma ray data and geochemical analyses are reported versus depth. The FMS images and the gamma ray data are used to identify the missing rock type(s). Then the geochemical analyses of recovered samples are used to calculate an average K_2O content for the core together with an average of K_2O content measured by the gamma ray tool over this specific depth interval.

new proportions for each lithology are calculated (Table 1) [Barr *et al.*, 2002]. A new average concentration is then calculated using the same chemical compositions and balanced by log-derived proportions (Figure 8, Table 1). The contents from the gamma ray logging tool were calculated by averaging all the measurements over an interval

specific to each core. (Figure 8, Table 1). If all the different lithologies were not recovered or analysed for a particular core, then average compositions of the different rock types were used instead. These calculations were performed on all cores for K_2O , except cores 3R and 13R because of their very low recovery (respectively 10% and 3.7%) (Table 2).

Table 2. Comparison, For Each Core, of K₂O Contents (wt%) and U Content (ppm) Extracted From the Logging Data (COLUMN “GAMMA-RAY”), CALCULATED FROM the Geochemical Analyses Using Core-Derived (Column “Core”) and Log-Derived (Column “Log”) Proportions and Using MST-NGR Data (K₂O and Tholeiitic Section Only)^a

Core	Length cored	K ₂ O					U					Non recovered material
		Recovery (%)	Gamma- ray	n	Core	n	Error	Gamma- ray	n	Core	n	
1R	9.3	79.9	2.59	62	0.26	2.51	16	0.25	2.61	0.52		40% breccia-60% altered massive basalt
2R	9.2	72.7	2.15	61	0.21	2.77	11	0.28	2.19	0.44		100% pillows
4R	9.5	25.5	0.53	60	0.05	0.02	3	0.00	0.57	0.11		50% breccia-50% hydrothermal
5R	9.3	68.4	0.71	64	0.07	1.83	24	0.18	1.28	0.26	68	100% massive basalt
6R	9.6	67.9	0.26	64	0.03	0.23	11	0.02	0.26	0.05	66	60% pillows-40% breccia
7R	9.4	62.5	0.29	61	0.03	0.18	14	0.02	0.28	0.06	61	100% breccia
8R	3.7	60	0.14	24	0.01	0.32	8	0.03	0.28	0.06	23	10% massive basalt
9R	5.8	100	0.10	41	0.01	0.06	10	0.01	-	0.10	58	100% recovery
10R	8.9	94.6	0.12	60	0.01	0.06	14	0.01	0.13	0.03	81	100% breccia
11R	9.4	45.2	0.42	62	0.04	0.15	11	0.01	0.43	0.09	43	70% pillows-30% breccia
12R	7.0	52	0.76	47	0.08	0.29	12	0.03	0.79	0.16	21	50% breccia-50% pillows
14R	9.7	66.2	0.70	62	0.07	0.38	6	0.04	0.74	0.15	45	100% sediment
15R	9.6	89.0	0.45	64	0.04	0.87	9	0.09	0.79	0.16	62	100% sediment
16R	9.5	70.7	0.53	64	0.05	0.47	7	0.05	0.55	0.11	50	30% breccia-70% pillows
17R	9.4	61.5	0.37	66	0.04	0.66	4	0.07	0.55	0.11	60	100% pillows
18R	9.5	30.4	0.25	62	0.02	0.40	3	0.04	0.25	0.05	32	90% pillows-10% breccia
19R	9.0	39.3	0.24	60	0.02	0.16	3	0.02	0.22	0.04	28	20% breccia-80% pillows
20R	9.3	31.9	0.40	60	0.04	0.53	3	0.05	0.40	0.08	33	90% pillows-10% breccia
21R	3.6	100	0.12	26	0.01	0.07	4	0.01	-	0.22	39	100% recovery
22R	8.3	47.6	0.26	56	0.03	0.26	2	0.03	0.25	0.05	28	90% pillows-10% breccia
23R	9.4	45.2	0.18	63	0.02	0.09	3	0.01	0.19	0.04	17	85% pillows-15% breccia
24R	9.4	38.9	0.27	63	0.03	0.30	4	0.03	0.28	0.06	17	85% pillows-15% breccia
25R	9.5	17.6	0.29	64	0.03	0.06	2	0.01	0.30	0.06	07	75% pillows-25% breccia
26R	9.5	24.1	0.33	62	0.03	0.19	5	0.02	0.33	0.07	34	70% pillows-30% breccia
27R	9.0	67.3	0.10	62	0.01	0.14	6	0.01	0.12	0.02	15	100% pillows
28R	9.2	48.9	0.18	61	0.02	0.28	4	0.03	0.25	0.05	23	100% pillows
29R	9.4	21.1	0.17	62	0.02	0.11	2	0.01	0.17	0.03	30	90% pillows-10% breccia
30R	9.3	85.2	0.14	61	0.01	0.17	4	0.02	0.17	0.03	18	100% pillows
31R	9.7	100	0.14	66	0.01	0.18	3	0.02	-	0.15	97	100% recovery
32R	9.4	19.9	0.58	62	0.06	0.92	3	0.09	0.68	0.14	35	100% pillows
33R	9.6	15.2	0.35	64	0.04	0.14	1	0.01	0.35	0.07	31	100% pillows
34R	9.6	52.7	0.23	64	0.02	0.24	4	0.02	0.23	0.05	36	75% pillows-25% massive basalt
35R	9.2	63.8	0.17	63	0.02	0.12	2	0.01	0.17	0.03	46	80% pillows-20% breccia
36R	9.2	78.8	0.31	60	0.03	0.18	3	0.02	0.31	0.06	57	60% breccia-40% pillows
37R	9.5	92	0.22	63	0.02	0.19	6	0.02	0.23	0.05	90	40% pillows-60% breccia
38R	9.4	58.3	0.29	63	0.03	0.17	3	0.02	0.29	0.06	50	10% pillows-90% breccia
39R	9.3	39.8	0.32	45	0.03	0.12	2	0.01	0.30	0.06	54	30% breccia-70% pillows

^a Columns “n” are the number of values (logging tool measurements or number of chemical analyses) used for the calculations. Columns “error” are estimated errors for each type of calculation (see text). Also reported are the lengths cored for each core (m), the recovery and the non-recovered material extracted from the core-log integration study.

Average U concentrations were calculated on 15 cores where enough chemical analyses were available (Table 2). Errors on this type of calculations are difficult to estimate as they depend on various factors. For the average compositions calculated using the core derived proportions the main sources of error are (a) the analytical error on the chemical analyses and (b) the identification of each lithology within the core and their proportions, calculated from the core images. The number of samples available per core for the calculations is an additional source of error as average compositions were used when all the lithologies were not analysed in a core. Errors on this set of calculations were estimated to be slightly higher than the analytical error and set at 10% (Table 2). For the second set of calculations, performed with the log-derived proportions, errors are to be higher than the previous ones, as they also depend on our ability to identify the missing lithologies. This also depends on the recovery, as the error on the un-recovered material will decrease with the recovery increasing. Errors for these concentrations were estimated to be twice higher than for the previous calculations and set at 20% (Table 2). Finally, errors on the logging data measurement alone are usually estimated to 10% for concentrations below 1% for K₂O and 10 ppm for U, which are the range of most of the Hole 801C basement section (Table 2).

4.2.4. MST-NGR Data

[29] For a comparison, we also calculated K₂O concentrations for each core using the MST-NGR data measured during Leg 185 [Plank *et al.*, 2000]. These were obtained simply by averaging all the data measured per core. We used the calibration defined during Leg 185 for K [Plank *et al.*, 2000] and applied it on the tholeiitic section of Hole 801C basement (Table 2).

5. Discussion

5.1. Can We Use Gamma Ray Data as a Proxy for Chemical Composition Downhole?

[30] The average K₂O contents per core, calculated with the core-derived proportions are more scat-

tered than those calculated using the log-derived proportions (Figure 9a). The latter plot closely on a one to one line, indicating a close agreement between the gamma ray data and K₂O contents calculated from the samples using the new proportions, adjusted for missing intervals (Figure 9a). The average concentrations per core, calculated using the MST-NGR data are also more scattered than those calculated using log-derived proportions. These concentrations plot close to the contents calculated using the core-derived proportions, although usually closer to the 1:1 line (Figure 9a). This result can be expected, as the MST-NGR data, measured on the recovered cores, also do not take into account the missing intervals. It demonstrates, however, the reliability of MST-NGR data and their close agreement with the chemical compositions of the samples. It also shows an averaging effect related to this type of data and comparable to the one observed for logging data. The volume of core analysed with the MST-NGR tool will be larger than the discrete sample measured by chemistry and therefore variations in the chemical compositions reported by the MST-NGR data will be less extreme.

[31] Most of the K₂O contents calculated with the core-derived proportions are lower than the content reported by the wire line logging tool (Figure 9a). This is related to two main effects: (a) the logging tool overestimates the K₂O contents or (b) using the core-derived proportions results in a bias against K₂O-rich rock types. The second explanation is likely as potassium will be more abundant in the most altered part of the basement section as well as in breccia and interpillow material [Alt *et al.*, 1998] and these brittle rock types are preferentially lost during drilling process [Brewer *et al.*, 1998, 1999]. It follows that average K₂O content of the cores will be underestimated if the core-derived proportions of the different rock types are used.

[32] It should be also noted, that some cores show average K₂O contents derived from the chemical analyses that are higher than the K₂O content reported by the logging tool (Figure 9a). This can be observed on both sets of calculations, using either core-derived or log-derived proportions and cannot be related to a bias in the lithological proportions. It

Figure 9. Plot of the average (a) K₂O (wt.%) content per core derived from the geochemical analyses versus the K₂O (wt.%) content per core derived from the gamma ray logging tool measurements and (b) U (ppm) content per core derived from the geochemical analyses versus the U (ppm) content per core derived from the gamma ray logging tool measurements. Each data point is representative of a core. The blue squares were calculated using the rock types proportions derived from the recovered cores and the pink circles were calculated using the lithology proportions derived from the core-log integration study. The yellow triangles reported on Figure 9a were calculated using the core-derived proportions and the MST-NGR data collected during Leg 185.

therefore must reflect a difference in the absolute K₂O content measured by the gamma ray tool and the chemical analyses. In this case, the question is whether the gamma ray logging tool underestimate the potassium content in the section or if the K₂O

contents measured on discrete samples and used for a specific lithology are an overestimation.

[33] Some samples, mainly breccia, display higher K₂O contents than measured by the logging tool,

Figure 10. Plot of K₂O contents of discrete samples and gamma ray data versus depth for the interval from 600 to 640 mbsf.

although the gamma ray curve does show peaks for these intervals (Figure 10, samples 185-801C-15R1-19-23 and 16R2-27-31, see also Figure 6). These samples comprise a matrix composed of highly altered basalt, carbonates, celadonite and clay minerals, preferentially enriched in K₂O, and a small proportion of basalt clasts. In contrast, the third breccia sample (Figure 9, 185-801C-16R5-62-65) is mainly composed of basaltic clasts (90%)

with only a small amount of matrix and its K₂O content is in close agreement with the tool measurement. This difference can either be related to the logging tool itself, which measures the gamma ray counts over a larger volume than the analysed sample or to the samples themselves. Some breccia and pillow basalts samples have extreme compositions and are probably not highly representative of the overall composition of these rock types in

the basement section. Other samples, in which basalt and matrix proportions are less extreme, are probably more representative of the overall composition (Figure 10). This can explain most of the differences observed between the chemical analyses and the gamma ray data for the pillow basalts, sediments and breccias (Figure 6). Despite uncertainties related to the radius of investigation of the tool and its averaging effect, this indicates that the gamma ray tool is well calibrated in basement sections and logging data can be used to accurately estimate the overall K_2O content in a borehole.

[34] The same features, as for K_2O , can be observed on the U calculations (Figure 9b). The average compositions per core calculated using core-derived proportions are slightly more scattered than those calculated using log-derived proportions. The latter also plot close to the one to one line (Figure 9b) and also demonstrate the reliability of the method. The concentrations calculated using the core-derived proportions are also slightly lower than the others and indicate the same bias toward U-rich lithologies, as observed on the K_2O calculations. The bias toward high concentrations observed for K_2O is not observed for U (Figure 9b, see also Figure 7). A ready explanation to this is found in the small contrasts in U concentrations between the different lithologies. The range of U concentrations in all lithologies are comparable and no extreme compositions are found in contrast to the K_2O data. The sample data are therefore probably more representative of the different lithologies. We can conclude that the gamma ray tool is also fairly well calibrated and that U data can be used as a further constraint on the chemical composition of a basement section.

[35] Despite relatively large errors on the calculations (up to 20%), mainly dependent on our ability to interpret the logging data and to recognise the missing lithologies, our results show that this method can be used with confidence to estimate the K_2O and U contents of a basement section. Furthermore, we demonstrate that the logging data are well calibrated and these results can be directly used to estimate the composition of the altered crust in term of K and U.

[36] This method also highlights the difficulty of choosing representative samples to use in a “composite” sample method. A major approach of ODP Leg 185 is to use such samples, which are a physical mixture of different rock types [Staudigel *et al.*, 1996; Plank *et al.*, 2000] to estimate the overall composition of the basement recycled in the Marianna subduction zone. The principal difficulty when preparing these composites will be first to choose the appropriate samples and then to choose in which proportions to mix them. If the samples are not representative of each rock type, but have extreme compositions, then neither of the core-derived or log-derived proportions will be representative. This is particularly critical for high K lithologies like breccia samples. Using the core-derived proportions may result in an underestimation of the concentrations but the use of log-derived proportions may also entrain an overestimation of the concentrations in the basement. However, the core-log-geochemical integration method is only applicable, so far, to two chemical elements, K and U in contrast to the composite sample approach which allow to analyse all the chemical elements as well as isotope compositions. A combination of these two methods is required to fully estimate the composition of the oceanic crust. This can be undertaken if samples are chosen to be representative of an average rock type by checking their composition against logging data and if enough samples of each rock type are analysed such that the range in composition is accurately represented. In this case, the log-derived proportions should be used to prepare the composite.

5.2. Oceanic Crust Composition and Impact on Flux Calculations

[37] The calculations performed enable average K_2O and U contents for the basement section drilled at Hole 801C to be calculated (Table 3). These estimates are important both for our understanding of the average composition of altered oceanic crust and in term of chemical fluxes recycled into subduction zones. For these two purposes we used two different estimates of the drilled section at Hole 801C. The upper alkali section is younger than the tholeiitic section and

Table 3. Summary of K₂O Contents (wt.%) and U Contents (ppm) Calculated From the Gamma Ray Data^a

	K ₂ O				U		
	Gamma ray data	Core-derived proportions	Log-derived proportions	MST-NGR ^b	Gamma ray data	Core-derived proportions	Log-derived proportions
Alkali upper sequence	2.10	2.54	2.11		1.29	0.98 ^d	1.14 ^d
Tholeiitic sequence	0.35	0.30	0.36	0.30	0.41	0.30	0.33
Tholeiite and alkali sections	0.47	0.34	0.51		0.50/0.42 ^c	0.34	0.39

^a The MST-NGR data and the average composition of each core reported in Table 1. The upper alkali lava sequence comprises mainly cores 1R and 2R. The logging data were used until 515 mbsf. The tholeiite sequence is from core 4R to 39R (logged interval).

^b MST-NGR data from core 5R to 39R.

^c 0.50 ppm represents the average of all U-gamma ray data over the logged interval while 0.42 ppm is the average of U-gamma ray data for the 15 cores used in the calculations.

^d These calculations comprise only core 2R.

may results from off axis magmatism. We therefore considered that only the tholeiitic section recovered was representative of a “normal” oceanic crust and could therefore be used to estimate the average composition of altered oceanic crust. On the other hand, to calculate the chemical fluxes recycled into the Marianna subduction zone we integrated the alkali basalts into the calculations as both these sections are to be subducted.

5.2.1. Composition of the Altered Oceanic Crust

[38] Previous calculations using NGT and MST-NGR data indicate average K₂O concentrations of 0.36 wt.% and 0.31 wt.% respectively for the tholeiitic section [Plank *et al.*, 2000]. We used the average core compositions (Table 2) to calculate new average K₂O and U contents for the tholeiitic sequence of Hole 801C (Table 3). The concentrations extracted from the gamma ray data values and calculated with the log-derived proportions are in very good agreement with respectively 0.35 wt.% and 0.36 wt.% for K₂O and 0.41 ppm and 0.33 ppm for U. Both K₂O and U concentrations calculated with the core-derived proportions are lower than those extracted from the gamma ray data or calculated with the log-derived proportions as well as K₂O concentrations calculated using average MST-NGR data (Table 3). As noticed before, the altered lithologies, such as breccia, are preferentially lost during the drilling and using core-derived proportions results in an underestimation of these rock types and an underestimation of the overall K and U contents down-

hole. The difference in average K₂O and U contents for the tholeiitic section is however relatively small given the errors associated with the various type of calculation (0.30 vs. 0.36 wt.% for K₂O and 0.30 vs. 0.33 ppm for U, Table 3).

[39] Overall, our results indicate that average K₂O content of altered oceanic crust is slightly higher than estimated from core-only geochemical calculations. More importantly, these values are different than those measured on the composite samples. The K₂O content of the “super composite” sample prepared during Leg 185 is 0.62 wt.% (Kelley *et al.*, submitted manuscript, 2002), which is much higher than our estimates but is comparable to the one reported for DSDP/ODP Sites 417 and 418 (K₂O 0.56 wt.%, [Staudigel *et al.*, 1996]). The difference is less significant in term of U as the concentration of the “super composite” sample is 0.39 ppm. These high values highlight the effects of choosing unrepresentative end-members samples with high K contents, which disproportionably increase the composite concentrations.

5.2.2. Recycled Crust Composition

[40] To estimate the K and U budget recycled to the Marianna subduction zone, the alkali upper section of Hole 801C basement must be taken into account as well as the tholeiitic section. We also calculated average K₂O and U concentrations for the alkali section and for the all basement section comprising the alkalic cap and the tholeiites of the logged interval (Table 3).

[41] Within the upper alkali section, the concentration calculated with the core-derived proportions is higher than the one derived from the logs or calculated from the log-derived proportions (Table 3). About 30% of the material was not recovered in this interval, and is interpreted as a mixture of pillows basalts and breccia. As the massive alkali basalts have higher K contents compared to pillow basalts and breccia, the average content of the sequence is lowered when using the log-derived proportions. All the average U concentrations calculated for the alkali sections are in good agreement. It should be noted, however, that these calculations comprise only one core (Table 3) and it is therefore difficult to extrapolate to the all section. For the all logged section (tholeiite + alkali basalts), the concentrations calculated using the core-derived proportions are lower than those calculated using both the log-derived proportions and the gamma ray data (0.34 wt.% vs. 0.51 wt.% and 0.47 wt.% respectively for K₂O and 0.34 ppm vs. 0.39 and 0.42–0.50 ppm respectively for U, Table 3).

[42] Although the difference induced by the recovery was small for the tholeiite section, the difference for the all basement is more significant. It shows that the use of core-derived proportions only may induce a bias of 20–50% in our estimates of the composition of the recycled crust.

[43] These results have significant implications for K and U budgets recycled into subduction zones. For the Marianna subduction zone a convergence rate of 4.75 cm/yr, over 2000 km can be assumed [Plank *et al.*, 2000]. Assuming an average density of 2.9 g/cm³ for the upper 500 m of oceanic crust, about 1.4 10⁴ g/yr are recycled. From our calculations, the associated K fluxes are 3.8 10³ g/yr using the core-derived proportions and 5.8 10³ g/yr using the log-derived proportions. The U fluxes calculated in the same manner are respectively 4.7 10^{−3} g/yr and 5.4 10^{−3} g/yr. K and U fluxes recycled into the subduction zone could therefore be higher than previously estimated, up to 20–50% for K and 10–20% for U. These results can also have strong implications for chemical fluxes between the altered oceanic crust and seawater and further work is needed to extend this approach and combine it to a composite sample approach to

access more chemical elements as well as the isotope compositions.

6. Conclusion

[44] In this paper we present a new approach to estimate the average composition of a drilled section by integrating core data, gamma ray wire line logging data and geochemical data. At ODP Site 801C a detailed core-log integration study was performed [Barr *et al.*, 2002], which allowed reconstruction of the complete basement stratigraphy. The FMS images together with other wire line logging data and images of the recovered cores were used to relocate the samples. We then calculated average K₂O and U contents of each core using the core-derived and log-derived rock types proportions and we compared them to the logging data. This approach have allowed us to demonstrate that the gamma ray tool (HNGS) is well calibrated against chemical analyses and MST-NGR data and enable to accurately determine the K₂O and U concentrations downhole. By using the wire line log-derived proportions we can account for the more strongly altered, K₂O and U-rich material, which is preferentially lost during drilling. The calculations undertaken in this study indicate that logging data are reliable enough to be used as a proxy for the K₂O and U concentrations of a borehole. We demonstrate that K and U fluxes are higher when log-derived proportions or gamma ray data are used instead of expanded core-derived proportions. The calculated fluxes are 20–50% higher for K and 10–20% higher for U.

[45] Our results indicate that K₂O concentrations and to a lesser extent U concentrations can be overestimated because inappropriate samples with extreme end-member compositions are often used. Composite samples should be prepared with extreme caution and this preparation integrated with wire line logging data to ensure that appropriate, representative samples of each rock type are combined in the correct, log-derived, proportions. In order to better constrain chemical fluxes between the oceanic crust and seawater as well as recycled into subduction zones, careful core-log-geochemical integration studies are essential.

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