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Stable isotopes: complementary data for assessing the biogeochemical cycling of elements in a remnant rear-arc basin - IODP Expedition 351

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Abstract

In June-July 2014, IODP Expedition 351 drilled 1461 m of a sedimentary sequence that records volcanic eruptions related to the subduction of the Pacific lithospheric plate under the Philippine Sea plate. The subduction-related volcanic debris have accumulated in the Amami-Sankaku Basin (ASB) for the last c. 50 million years, and now sit below the Philippine Sea at a water depth of 4700 m. In the sediments of the ASB, water-rock interactions and the biological activity of prokaryotes (Bacteria and Archaea) are contributing for the release (to the ocean) of chemical elements that were originally trapped in the minerals and volcanic ash that once were erupted from deep in the Earth's mantle. On the other hand, the formation of secondary minerals and sorption reactions are contributing for the retention of other chemical elements in this basin. Due to their fractionation during biogeochemical reactions, stable isotopes of chemical elements such as oxygen, carbon and sulphur are very important to better understand the cycling of elements. The results attained so far reveal a relatively low abundance of prokaryotes and a very low sulphate-reducing bacterial activity in the drillsite U1438, in the ASB. In addition, the deeper interstitial waters of this drillsite have ^{18}O-enriched dissolved sulphate which may indicate isotopic exchange of oxygen in sulphate with oxygen in the water molecules which, in turn, are influenced by the interaction with ^{18}O-rich minerals and also interaction with relic andesitic magmatic water.

Introduction

Geological setting of Site U1438

IODP Expedition 351 was held in June-July 2014, at Site U1438, with the main scientific objective of recovering the geological record related to the early evolution of the Izu-Bonin-Mariana (IBM) intraoceanic arc, contributing to advance our understanding of subduction initiation and continental crust formation. Site U1438 is located in the Amami Sankaku Basin (ASB), <100 km west of the northern portion of the Kyushu-Palau Ridge (KPR) which is a remnant arc of the intraoceanic IBM arc in the western Pacific (Figure 1). The ASB preserves a sequence of volcaniclastic sediments and tephra that record the volcanic eruptions related to the subduction of the Pacific lithospheric plate under the Philippine Sea plate during the last c. 50 million years (Arculus et al. 2015).

In Site U1438, at a water depth of 4700 m, IODP Expedition 351 drilled a 1461 m-long volcaniclastic sequence from ASB, and 150 m of the underlying oceanic crust, with a recovery of 1182 m of volcaniclastic sediments and 44 m of oceanic crust. In the upper 950 m of the volcaniclastic sequence, a total of 67 interstitial water samples were taken from whole rounds at almost every 9.5 m-long core.
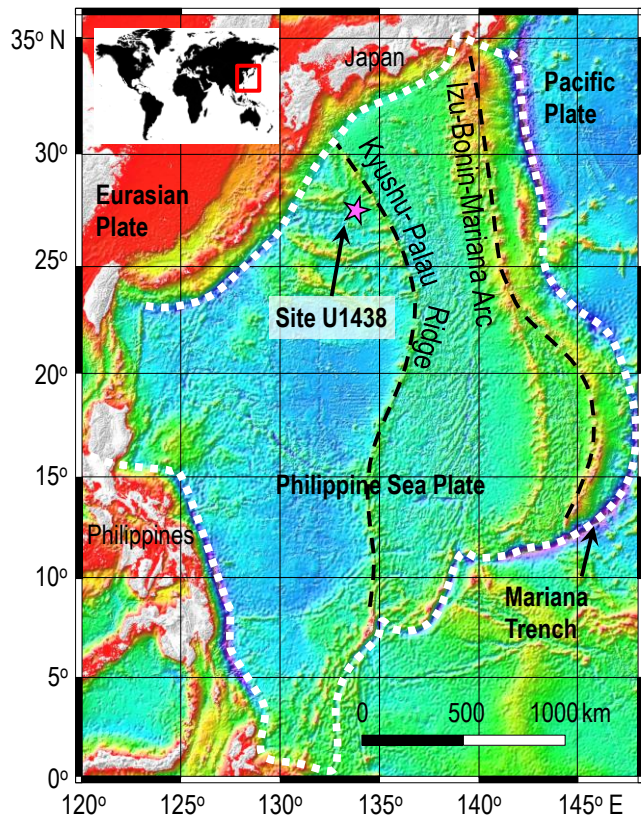
Figure 1 – Location of Site U1438. Dashed white line – Philippine Sea Plate boundary; bathymetry: red < 100 m, purple > 10.000m. Modified from Arculus et al. (2015).

According to Arculus et al. (2015), the volcaniclastic sequence recovered in Site U1438 was divided in four lithostratigraphic units and one additional unit comprising the underlying oceanic crust. In Table 2, the main characteristics of each lithostratigraphic unit are briefly described and in Figure 2 photographs of selected core sections are shown to illustrate the different lithologies drilled.

Table 1 – Lithostratigraphic summary of Site U1438 (from Arculus et al., 2015). Notes: N/A – Not applicable

| Unit	Thickness	Lithology	Age
I	160.3	Terrigenous, biogenic, and volcaniclastic fine sediments	Recent to latest Oligocene to Pleistocene (23 to 0 Ma)
II	149.3	Tuffaceous mudstone, siltstone, and fine sandstone	Oligocene (34 to 23 Ma)
III	1051.8	Tuffaceous mudstone to coarse sandstone and tuffaceous breccia-conglomerate	Eocene to Oligocene (55 to 34 Ma)
IV	99.7	Radiolarian-bearing mudstone	Eocene (≈ 58 to 55 Ma)
1	N/A	Lava flows composed of sparsely vesicular, microcrystalline to fine-grained, aphyric to sparsely porphyritic basalt	Eocene (?)
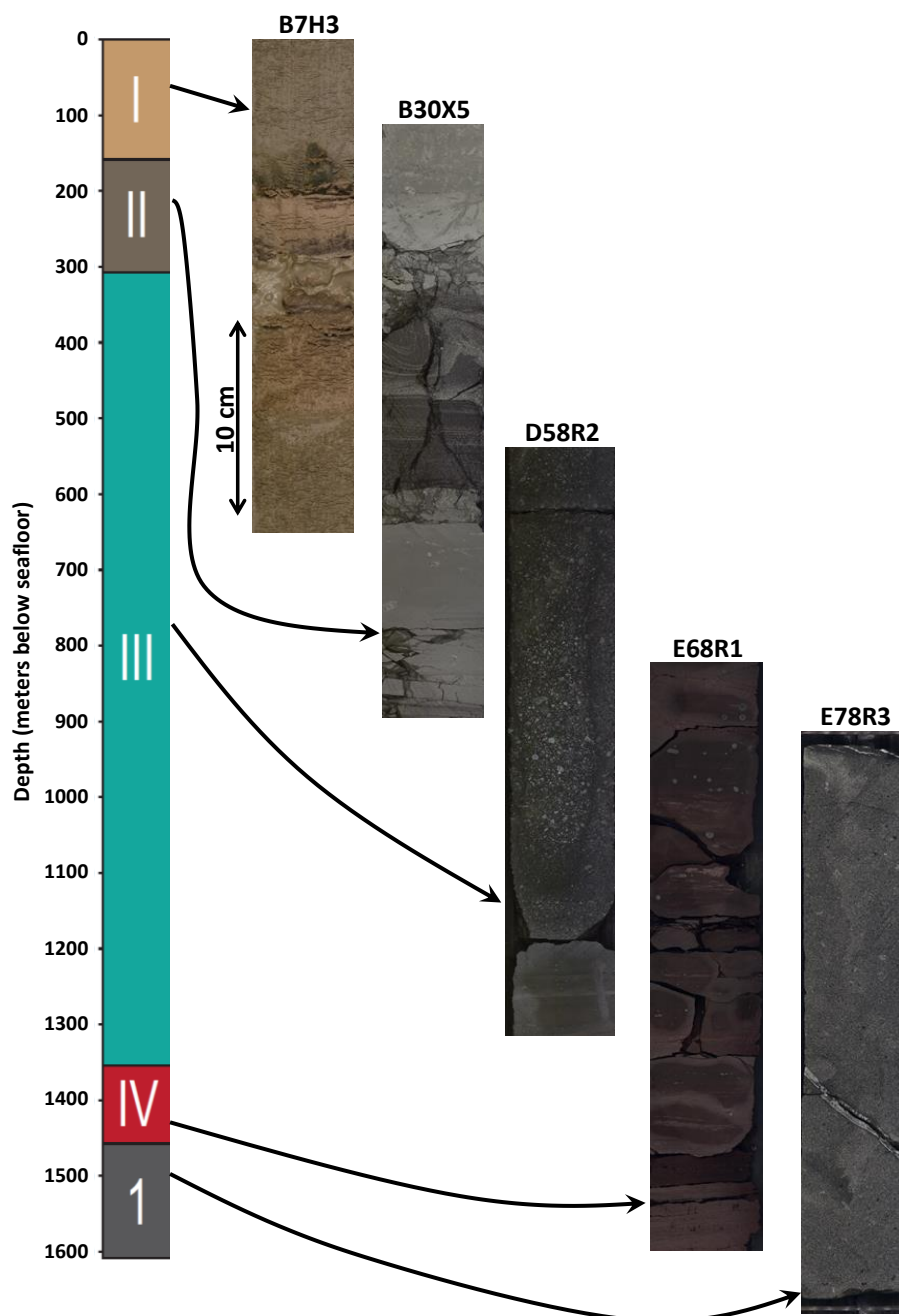
Figure 2 – Lithostratigraphic column defined for Site U1438 and photographs of selected core sections to illustrate the different lithologies drilled.

The study of stable isotopes to assess biogeochemical reactions

Stable isotopes of oxygen, carbon and sulphur are important tools to decipher the relative importance of geochemical reactions that lead to the dissolution of primary minerals and to the formation of secondary minerals. In addition, geochemical reactions involving changes in the redox state of these elements which are triggered by microbial activity, mainly respiration and fermentation, can also be assessed based on the distribution of these isotopes in different solutes and minerals (Clark & Fritz 1997).

Previous studies focused on the stable isotopes of sulphur and oxygen in dissolved sulphate from interstitial waters of marine/estuarine sediments have shown that when sulphate is reduced by sulphate reducing bacteria (SBR), and elemental sulphur (S(0)) is disproportionated to sulphate

(S(VI)) and sulphide (S(-II)), the sulphate remaining in solution will be progressively enriched in the heavier isotope ^{34}S (Werne et al. 2003). In addition, if some dissolved sulphate is originated by oxidation of sulphide, the $\delta^{18}O_{SMOW}$-SO_4^{2-} (SMOW stands for Standard Mean Ocean Water) usually decreases relative to the average seawater value of +9.7‰ (Mandernack et al. 2003).

Ocean water has an average $\delta^{13}C_{PDB}$-DIC (Dissolved Inorganic Carbon) of approx. 0‰ which is consistent with the chemical equilibrium between ocean water and marine carbonates (PDB stands for the Pee Dee Belemnite International Standard). In addition, biodegradation of organic carbon produces ^{13}C-depleted CO_2, because prokaryotes preferentially break the lighter isotope-bearing organic matter molecules. $\delta^{13}C_{PDB}$-CH_4 of biogenic origin is usually lower than -40‰ while the abiogenic methane (thermogenic or mantle-derived) has $\delta^{13}C_{PDB}$-CH_4 values between -40 and -10‰. Methane, when oxidized to CO_2, contributes to lower the $\delta^{13}C_{PDB}$-DIC. Carbonate minerals in igneous and metamorphic rocks may have $\delta^{13}C_{PDB}$ between -15 and 15‰ (Clark & Fritz 1997).

In a volcaniclastic sedimentary basin, ^{18}O and ^{2}H of the interstitial water are mainly influenced by water-rock interactions such as isotopic exchange with primary silicate minerals, formation of hydrated secondary silicate minerals, and the eventual dissolution of these minerals. The isotopic exchange between water and primary silicate minerals, which are rich in ^{18}O, will lead the interstitial water to heavier values. Nevertheless, the hydration of silicate minerals with the formation of clays and zeolites will contribute for a depletion of the residual interstitial water in ^{18}O. The reverse occurs for ^{2}H where interlayer water of the clays' structure tends to become depleted in ^{2}H, leaving the interstitial water enriched in this isotope (Clark & Fritz 1997).

To study the biogeochemical cycling of chemical elements in Amami-Sankaku Basin, selected samples of interstitial waters and volcaniclastic rocks from IODP Expedition 351, as well as samples of the drilling muds used in this expedition, were analysed in the University of Salamanca (Spain) for their content in stable isotopes, as described in Table 2, below:

Table 2 – Sample types and stable isotopes analysed in the University of Salamanca in the frame of the ECORD Research Grant.

Sample type	Molecule/mineral	Stable Isotopes	Number of samples analysed
Interstitial water from U1438	SO_4^{2-}	$^{34}S/^{32}S$, $^{18}O/^{16}O$	18
	H_2O	$^{18}O/^{16}O$, $D/^1H$	4[a]
	Dissolved Inorganic Carbon (DIC)	$^{13}C/^{12}C$	12[a]
Sedimentary rocks from U1438	Carbonate minerals, mainly calcite	$^{13}C/^{12}C$, $^{18}O/^{16}O$	1
	Barite, and Gypsum/Anhydrite	$^{34}S/^{32}S$	1
	Silicate minerals and Fe/Mn oxyhydroxides	$^{18}O/^{16}O$	8
Drilling muds (barite and sepiolite)	Carbonate minerals, mainly calcite	$^{13}C/^{12}C$, $^{18}O/^{16}O$	2
	Barite, and Gypsum/Anhydrite	$^{34}S/^{32}S$, $^{18}O/^{16}O$	3

[a] At the moment of submission of this report these analyses were not completed.

Methods

Separation of SO_2 gas for the analysis of $^{34}S/^{32}S$

The sedimentary rock sample D15R2 from Site U1438 and the drilling muds used in Expedition 351 (barite-rich mud and sepiolite-rich mud) were analysed for the stable isotopes $^{34}S/^{32}S$ and $^{18}O/^{16}O$ in sulphate minerals, in the Laboratory of Stable Isotopes of the University of Salamanca. Two types of sulphate minerals were extracted from each sample: (1) barite ($BaSO_4$) which is the less soluble sulphate, and (2) gypsum and anhydrite which are more soluble.

In the laboratory, the samples were crushed to very fine grain size, and then digested with 6N hydrochloric acid (HCl), in a proportion of 10 g of sample for 10 mL of HCl (step 1 in Figure 3). Each sample with HCl was heated at 80ºC for approximately one hour. Afterwards, the sediment suspension was filtered (step 2 in Figure 3) and the retained sediment with barite and other HCl-resistant minerals were weighted and packed for the S and O vacuum lines (Figure 4), while the filtrate with dissolved gypsum and anhydrite was prepared following the procedure described in Clark & Fritz (1997) for dissolved sulphate.
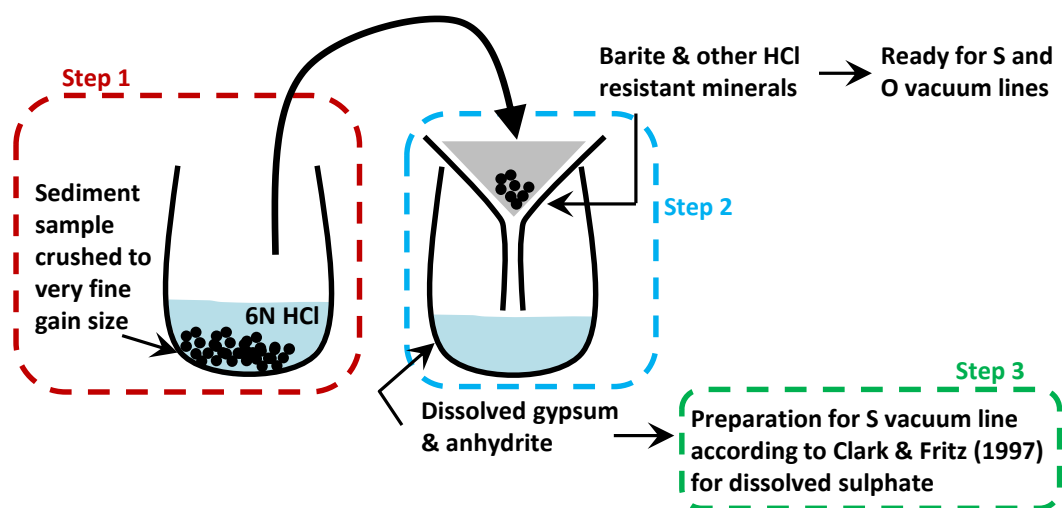

Figure 3 – Sketch of the laboratory procedure followed for sediment sample preparation for the analysis of S stable isotopes.

After the preparation of the sediment samples, as shown in Figure 3, the samples which were under processed to obtain $BaSO_4$-rich powder were mixed with copper oxide and quartz-rich powders and inserted in a glass container which was placed in the combustion oven (Figure 4) to attain 1148ºC. As soon as this temperature was reached the gas released from the combusted sample entered the S vacuum line where it experienced a series of steps with changing temperatures in order to separate the SO_2 gas from the other gases and retain this SO_2 gas in the final container (at the right-side of the S vacuum line in Figure 4).
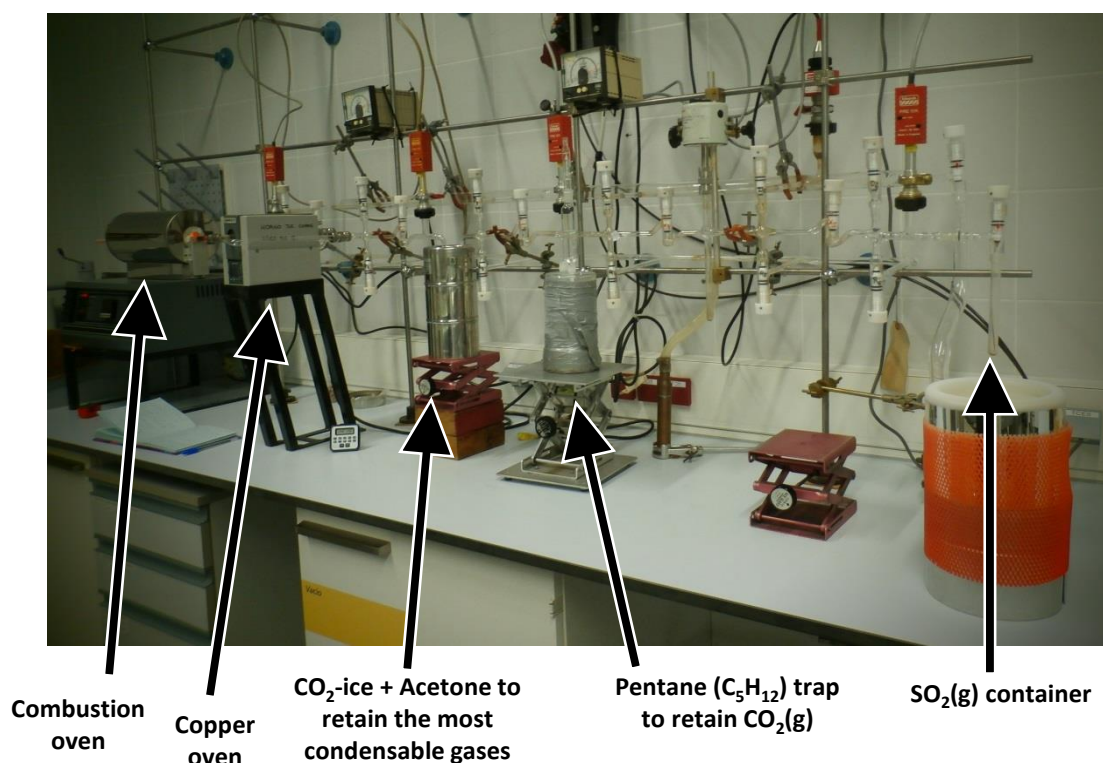
Figure 4 – S vacuum line in the Laboratory of Stable Isotopes of the University of Salamanca.

Separation of CO$_2$ gas for the analysis of ^{13}C/^{12}C in sediment samples

The sedimentary rock sample from U1438 and the drilling muds samples analysed for the stable isotopes ^{13}C/^{12}C and ^{18}O/^{16}O in carbonate minerals were crushed to very fine grain size, and then digested with phosphoric acid (H$_3$PO$_4$) at approximately 25ºC during 24H. Then, the container with the digested sediment sample was inserted in the C vacuum line to extract the CO$_2$ gas for subsequent analysis of ^{13}C/^{12}C.

Results and Discussion

The results obtained for δ^{34}S$_{CDT}$ and δ^{18}O$_{SMOW}$ in dissolved sulphate and sulphate minerals are presented in Table 3 and Figure 5. The interstitial water samples that were used for these analyses are from different sub-samples that were done onboard Expedition 351: ORP, PA and SENA (first column of Table 3). In order to assess the possible influence of the different procedures used in each interstitial water sub-sample on the results of stable isotopes composition, the three sub-samples of sample B4H4 were analysed for ^{34}S/^{32}S and ^{18}O/^{16}O. The results show that there is a variation of 0.70‰ for δ^{34}S$_{CDT}$ and 0.73‰ for δ^{18}O$_{SMOW}$, within the three sub-samples. Since the sub-sample used in each interstitial water analysed for ^{34}S/^{32}S and ^{18}O/^{16}O was not always the same, the variation observed within the three sub-samples must be taken into account, and therefore, a precision of ±0.35‰ for δ^{34}S$_{CDT}$ and ±0.37‰ for δ^{18}O$_{SMOW}$ should be considered in the results presented and discussed in the next paragraphs.

Table 3 – Stable isotopes ^{34}S/^{32}S and ^{18}O/^{16}O, expressed in the delta notation, analysed in dissolved sulphate and sulphate minerals from Site U1438 and the drilling muds used in this site.

Sample Ref.	Sample depth (mbsf)	Sample Type	Lithological Unit	$\delta^{34}S_{CDT}$ (‰)	$\delta^{18}O_{SMOW}$ (‰) ±1σ
Seawater	-	Seawater at the surface	-	21.2	9.10±0.15
B1H4 ORP	2.9	Interstitial water	I	20.8	8.37±0.20
B4H4 ORP	32.1	Interstitial water	I	20.6	9.88±0.14
B4H4 PA	32.1	Interstitial water	I	21.0	10.23±0.10
B4H4 SENA	32.1	Interstitial water	I	21.3	9.61±0.01
B12H4 SENA	108.05	Interstitial water	I	22.4	8.51±0.26
B17H5 PA	157.05	Interstitial water	I	22.3	10.21±0.04
B18H3 PA	163.55	Interstitial water	II	22.8	10.41±0.06
B20F2SENA	171.75	Interstitial water	II	22.2	10.40±0.23
B23X3 ORP	184.95	Interstitial water	II	21.8	9.99±0.57
D11R1 ORP	297.8	Interstitial water	II	22.9	11.81±1.07
D39R5 PA	574.77	Interstitial water	III	24.0	12.54±0.27
D40R5 PA	583.65	Interstitial water	III	21.0	14.36±0.04
D60R6 PA	779.46	Interstitial water	III	21.9	
D62R2 PA	792.44	Interstitial water	III	22.1	9.78±0.29
D15R2-Y	337.63	Sedimentary rock (gyps+anhy)	III	20.1	11.26
Sep-Y	-	Drilling mud (gyps+anhy)	-	26.5	14.70±0.08
BM-Y	-	Drilling mud (gyps+anhy)	-	26.5	13.97±0.03
Barite-mud	-	Drilling mud	-	27.2	14.24±0.31
NBS-127	-	Reference material	-	21.0 (21.1)	

Notes: CDT – Cañon del Diablo Troilite International Standard; SMOW – Standard Mean Ocean Water; values in parenthesis are the reported values for the reference material NBS-127.

In a sedimentary basin where SRB are present and active, the dissolved sulphate that is left behind will progressively acquire more positive values of $\delta^{34}S_{CDT}-SO_4^{2-}$ with respect to the seawater value (c. 21‰), because SRB preferentially break-down the lighter isotope-bearing sulphate molecules (Mandernack et al. 2003). Dissolved sulphate in the interstitial waters of Site U1438 shows downward decreasing concentration, from seawater values to 14 mM, and has a range of $\delta^{34}S_{CDT}$ between 20.6 and 24.0 ±0.35‰ which possibly indicates a relatively low rate of sulphate-reducing bacterial activity and sulphate mineral precipitation such as gypsum and anhydrite, confirmed by onboard mineralogical analyses and preliminary calculations of the corresponding saturation indices.

From the top of the sedimentary column until approximately 30 meters below seafloor, the interstitial waters have a $\delta^{34}S_{CDT}-SO_4^{2-}$ value very similar to seawater. Then, at the top of lithostratigraphic Unit II, a heavier $\delta^{34}S_{CDT}-SO_4^{2-}$ value is recorded; 22.9 ±0.35‰. In Unit III, the heaviest analysed value of 24.0 ±0.35‰ is recorded in section D39R5, at 575 mbsf (Figure 5). The sedimentary rock sample collected in section D15R2 which is a tuffaceous sandstone/breccia rich in plagioclase, pyroxene, oxide minerals, and zeolites has a $\delta^{34}S_{CDT}$ of 20.1‰ in the more soluble sulphate minerals gypsum and anhydrite which is very similar to the present seawater value.
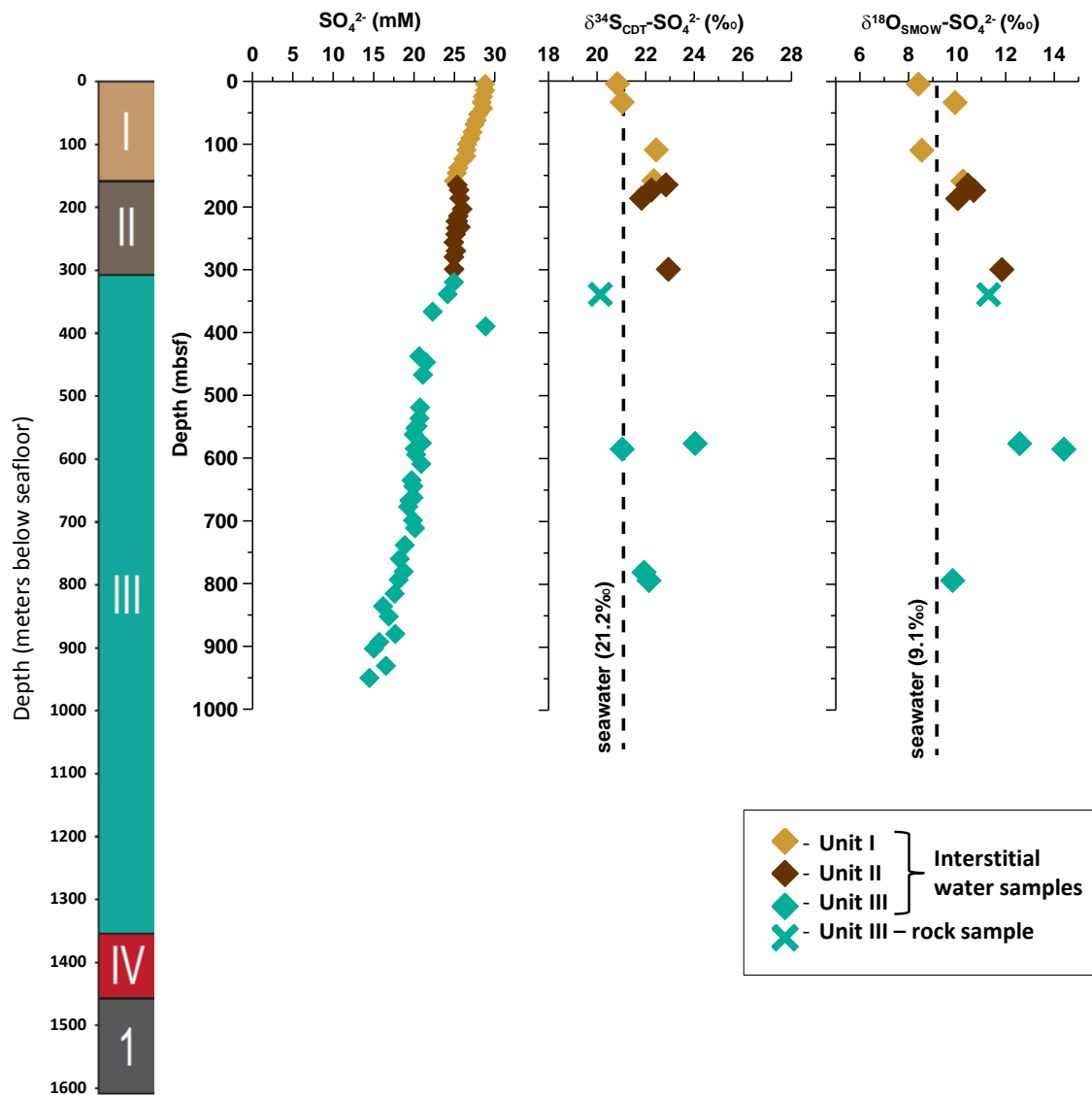
Figure 5 – Depth profiles of dissolved sulphate (from Arculus et al. 2015), $\delta^{34}S_{CDT}$-SO_4^{2-} and $\delta^{18}O_{SMOW}$-SO_4^{2-} for the interstitial water samples and sedimentary rock sample D15R2 collected in Site U1438.

By plotting $\delta^{34}S_{CDT}$-SO_4^{2-} against $\delta^{18}O_{SMOW}$-SO_4^{2-} for the interstitial water samples collected in Site U1438 it is possible to see that there are two samples from Unit I that are closest to the isotopic composition of seawater (Figure 6). These are samples B1H4 and B4H4 which are the shallowest interstitial water samples and are hydraulically connected to present-day seawater. Dissolved sulphate in the interstitial water samples of Unit II has heavier oxygen and sulphur isotopic composition than seawater which may indicate that:

- Sulphate reduction and precipitation of sulphate minerals like gypsum and anhydrite may be preferentially consuming the lighter sulphur isotopes, contributing for a progressive increase of $\delta^{34}S_{CDT}$-SO_4^{2-}

- Oxygen from dissolved sulphate may have undergone isotopic exchange with the interstitial water which in turn may be influenced by the combined effect of the relatively low water-rock mass ratio, the interaction with ^{18}O-enriched minerals and the interaction with relic andesitic magmatic water (Giggenbach 1992)

The isotopic composition of dissolved sulphate in the interstitial water samples of Unit III shows a higher range of values of $\delta^{34}S_{CDT}$-SO_4^{2-} than the samples from the other lithostratigraphic units (Figure 6). In addition, the interstitial water sample D40R5 has a relatively high $\delta^{18}O_{SMOW}$-SO_4^{2-} of 14.36 ±0.37‰ which may indicate the influence of the same processes already described for Unit II, but with a more pronounced effect.
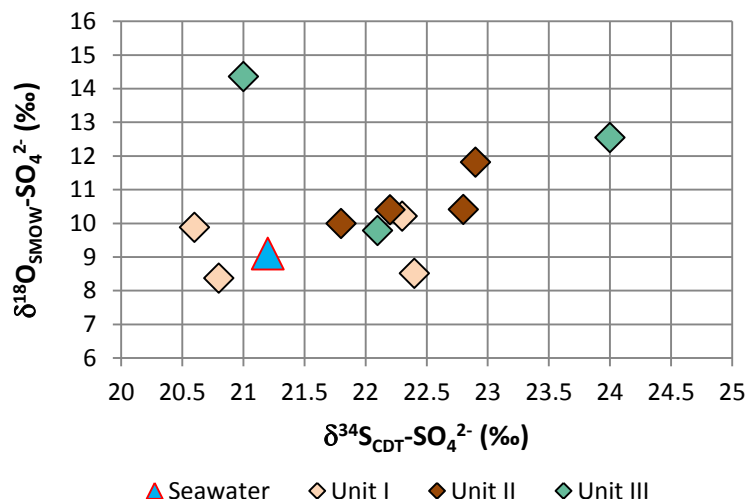

Figure 6 – Oxygen and sulphur isotopic composition of the seawater and interstitial water samples from IODP Expedition 351.

In Table 4, the results obtained for $\delta^{13}C_{PDB}$, $\delta^{18}O_{PDB}$ and $\delta^{18}O_{SMOW}$ in carbonate minerals are presented. The sedimentary rock sample E66R2 collected at 1448.13 mbsf corresponds to the white mineralized vein (in Figure 7) which has a mixture of calcite, chlorite, zeolites and clay minerals, according to shipboard results (Arculus et al. 2015). This sedimentary rock sample was collected relatively close (13 m) to the bottom of ASB which sets on basaltic lava flows of the oceanic crust. $\delta^{18}O_{SMOW}$-carbonates of sample E66R2 is not typical of marine carbonates, and probably indicates that these are derived from hydrothermal fluids.

Table 4 – Stable isotopes of $^{13}C/^{12}C$ and $^{18}O/^{16}O$, expressed in the delta notation, analysed in carbonate minerals of one sample from Site U1438 and the drilling muds used in this site.

Sample	$\delta^{13}C_{PDB}$ (‰)	$\delta^{18}O_{PDB}$ (‰)	$\delta^{18}O_{SMOW}$ (‰)	Sample depth (mbsf)
E66R2	-3.09	-17.95	12.41	1448.13
Sepiolite	-2.93	-10.50	20.08	-
Barite-mud	-5.69	-9.52	21.10	-
Reference EEZ-1	2.43 (2.39)	-4.67 (-4.83)	26.10 (25.92)	-

Note: values in parenthesis are the reported values for the reference material EEZ-1.

Figure 7 – Photograph of the location of sample E66R2 (scale is in centimetres).

In Table 5, the results obtained for $^{18}O_{SMOW}$ in whole rock samples and mineralized veins are presented. The whole rock sample D15R2 has a value that is within those observed in basaltic rocks, while the value obtained in sample E5R2 is more typical of metamorphic rocks. This may indicate that the water-rock interactions in ASB, which are within temperature-pressure conditions of low-grade metamorphic processes, are shifting the original igneous isotopic composition of the tuffaceous materials towards heavier isotopic signatures. The results obtained in mineralized veins show that the sulphate-rich vein has a much heavier oxygen isotopic signature (22.9‰ in sample E13R5) than the silicate-rich vein (6.1‰ in sample E66R2).

Table 5 – Stable isotopes of $^{18}O/^{16}O$, expressed in the delta notation, analysed in whole rock and mineralized vein samples from Site U1438 and the sepiolite-rich drilling mud used in this site.

Sample Ref.	Sample depth (mbsf)	Sample Type	Lithological Unit	$\delta^{18}O_{SMOW}$ (‰)
D15R2	337.63	Whole rock – tuffaceous conglomerate	III	12.4
E5R2	879.21	Whole rock – tuffaceous sandstone	III	20.1
E13R5	960.21	White vein with some gypsum & anhydrite	III	22.9
E66R2	1448.13	white vein, 20% zeolites & plagioclase + 5% carbonates	IV	6.1
E68R1	1456.38	Reddish mudstone (rich in Mn & Fe oxides)	IV	12.4
Sepiolite	-	Drilling mud	-	17.4

Acknowledgements

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Balanced Budget

In the Table below, the expenses incurred in the frame of the ECORD Research Grant are described:

Travel, Accommodation and meals for a stay of 23 days in the Stable Isotopes Laboratory of the University of Salamanca	Laboratory analyses	TOTAL COSTS
629.92 EUR	1368.51 EUR	1998.43 EUR