

# Europlanet TNA Report – 079-TNA3 (Smet)

## PROJECT LEADER

<b>Name:</b> <a href="#">Ingrid Smet</a>
<b>Address:</b> <a href="#">Ghent University</a> <a href="#">Department Geology and Soil sciences</a> <a href="#">Mineralogy and Petrology</a> <a href="#">Krijgslaan 281 - S8</a> <a href="#">9000 Ghent</a> <a href="#">Belgium</a>
<b>E-mail:</b> <a href="mailto:Ingrid.Smet@ugent.be">Ingrid.Smet@ugent.be</a>

## COLLABORATORS

<b>Name:</b>	<b>Affiliation:</b>
<a href="#">Dr. Marlina A. Elburg</a> (main supervisor)	<a href="#">School of Geological Sciences, University of KwaZulu-Natal, Durban, South Africa</a>
<a href="#">Dr. Peter Van den haute</a> (co-supervisor)	<a href="#">Department Geology and Soil sciences, Ghent University, Belgium</a>
<a href="#">Dr. Frank Vanhaecke</a> (co-supervisor)	<a href="#">Department Analytical Chemistry, Ghent University, Belgium</a>
<b>Date of TNA visit:</b>	<a href="#">From 11 November 2012 to 4 December 2012</a>
<b>No. of access days:</b>	<a href="#">17</a>
<b>No. of days stay:</b>	<a href="#">25</a>
<b>Host laboratory:</b>	<a href="#">Vrije Universiteit Amsterdam, VUA, Isotope Geochemistry Facility (C8)</a>
<b>Reimbursed</b>	<a href="#">Yes/No</a>

**Geochemical investigation into the volcanic rocks from the  
westernmost part of the South Aegean arc:  
whole rock  $^{176}\text{Hf}/^{177}\text{Hf}$  analyses**

**Scientific Report Summary.**

*(plain text, no figures, maximum 250 words, to be included in database)*

Geochemical and petrological research into the volcanic rocks from the westernmost part of the South Aegean arc indicates that the identity of sources and processes involved in magma genesis are obscured by later-stage intensive magma mingling and - mixing. Only whole rock Pb isotopic data and the Hf isotopic compositions of zircons derived from these volcanic deposits indicate a more systematic variability amongst the magma sources for the 3 volcanic centres. Whole rock  $^{176}\text{Hf}/^{177}\text{Hf}$  analyses of host rocks and enclaves would allow further investigation of this variability and be a valuable extra parameter to constrain the characteristics of different sources involved in the magma genesis of arc lavas in this part of the Aegean arc.

The magnitude of dissolution-related Hf blanks was investigated at Ghent University prior to the visit to the VUA Isotope Geochemistry Facility. Since blanks were less than 0.05 ng and thereby negligible compared to the typical sample size of 100-1000 ng, 38 zircon-bearing samples were digested at higher pressure in Parr bombs, and 45 zircon-free samples at atmospheric pressure with HF/HNO<sub>3</sub>/HCl.

These samples were then brought to Amsterdam where the Hf isolation was successfully carried out for all 83 samples. However, due to malfunctioning of the MC-ICP-MS these Hf fractions could not yet be analysed.

Measurement of the  $^{176}\text{Hf}/^{177}\text{Hf}$  is therefore postponed to the first half of 2013, and, based on the Hf concentration data from these fractions they are expected to shed light on the identity of potentially different sources and processes involved in the magma genesis of these volcanites.

## Full Scientific Report on the outcome of your TNA visit

Approx. 1 page

### *Introduction & aims*

Whole rock (WR) major and trace element data of the three volcanic centres Aegina, Methana and Poros, located in the westernmost part of the South Aegean active volcanic arc, indicate that geochemical trends are dominated by magma mixing, obscuring the influence of other processes (e.g., fractional crystallization, assimilation,...) involved in magma genesis. Whole rock Sr and Nd isotopic data also show scattered trends which overlap for all three volcanic centres. This points towards a complex combination of different sources responsible for magma genesis but also reveals significant crustal contamination. However, whole rock Pb isotopic data seem to be de-coupled from the Sr-Nd isotopic system and suggest distinct trends for the different volcanic centres and phases. Laser-ablation Hf isotopic analyses on magmatic zircons collected from 11 volcanites also seem to indicate a certain isotopic distinction between the three volcanic islands.

Higher-precision whole rock  $^{176}\text{Hf}/^{177}\text{Hf}$  analyses of host rocks and enclaves from these 3 volcanic centres would allow further investigation of this variability and be a valuable extra parameter to constrain the characteristics of different sources involved in the magma genesis of arc lavas in this part of the Aegean arc. Since these geochemical analyses are not set up at Ghent University, the 079-TNA3 project provided for Hf isolation and subsequent  $^{176}\text{Hf}/^{177}\text{Hf}$  isotopic measurements at VUA Isotope Geochemistry Facility, Amsterdam.

### *Results*

Sr, Nd and Pb isotopic ratios for the volcanites sampled from Aegina, Methana and Poros, were used to select the samples that would be prepared for Hf isolation at the VU. Prior to this, a full set of blanks was collected and analysed from both the high pressure (HP: Parr bombs, 180°C, for zircon bearing samples) and low pressure (LP: HF/HNO<sub>3</sub>/HCl, 110°C, for zircon-free samples) digestion procedure to estimate their potential contribution to the Hf concentrations. This showed however that only negligible amounts of Hf would be derived from acids and containers (less than 0.05 ng, whereas at least 100 ng Hf was expected to be present in the samples) – so that by July 2012 the HP digestion of 38 (samples + rock standards + full procedure blanks + duplicate sample) was initiated at Ghent University. The number of samples digested under high pressure conditions was hereby limited to the number of Parr bombs (4) present at Ghent University. 45 more (samples + rock standards + full procedure blanks + duplicate sample) were digested by standard low pressure acid dissolution at the end of October. Once all 83 samples were dissolved and dried down, they were redissolved in 2mL 6N HCl, and again dried down to facilitate redissolving them at the VU in 3N HCl prior to Hf isolation.

A selection of 50-60 samples was made prior to arriving at the VU because the time seemed limited for the isolation of 80+ samples. Nevertheless Hf isolation for all 83 samples was carried out between Monday the 12<sup>th</sup> and Thursday the 29<sup>th</sup> of November. The 83 Hf fractions were subsequently redissolved in 1mL, of which 50µL was used to determine the exact Hf concentration in each of the Hf fractions by quadrupole ICP-MS. These analyses were finalised by Tuesday the 4<sup>th</sup> of December, and showed that for all samples enough Hf was recovered (at least 100ng) to allow for isotopic measurement on the MC-ICP-MS.

### *Problems*

Due to a technical defect in the MC-ICP-MS's interface, it was not possible to obtain the right vacuum conditions necessary for analyses. Since this problem could not be solved within the time scheduled for my work at the VUA, I returned to Ghent 4 days earlier than initially planned (on Tuesday the 4<sup>th</sup> of December instead of Saturday the 7<sup>th</sup>).

### *Future work*

Since all 83 samples were successfully prepared for Hf isotopic measurement, they are now stored at the VUA where they will be analysed on the MC-ICP-MS at a later date (probably late winter/early spring 2013). I will therefore have to return to Amsterdam once more for about 5 working days (allowing for technical difficulties during set-up and tuning of the MC-ICP-MS instrument for  $^{176}\text{Hf}/^{177}\text{Hf}$  analyses).

### *Expected results*

Amongst the 83 Hf fractions are both LP and HP digestions for the 11 samples of which LA-MC-ICPMS zircon Hf isotopic data were already obtained. Comparison of the Hf concentrations between these two digestion types shows important systematic differences (see Table 1) – reflecting the non-dissolution of zircon during the LP procedure. Isotopic fingerprinting of these LP and HP Hf fractions, together with the zircons' Hf isotopic signature, will show whether one or more magma sources gave rise to these volcanites and their enclaves.

Comparison of the WR Hf isotopic data for the three volcanic centres will furthermore allow better understanding of the origin and development of sources involved in the different volcanic phases in the westernmost part of the South Aegean arc.

### *Planned publications*

These WR Hf isotopic data represent the final analyses for my PhD research into the geochemistry and petrology of the westernmost part of the South Aegean active volcanic arc. They will therefore definitely be published in one of the (later) papers presenting, discussing and interpreting the large geochemical data set collected over the last years from Methana, Aegina and Poros.

### *Host approval*

Prof. Gareth Davies communicated via e-mail his approval of this report:

'The report is excellent and I give approval to send it on to Beverley at the OU.'

Sample information		Hf isolated at VUA (ng)	
		HP digestion	LP digestion
	<b>STANDARDS</b>		
LP full procedure blank	LP BLK (1)	<i>Not distinguishable from the Hf content of the final dilution acid</i>	
LP full procedure blank	LP BLK (2)		
LP full procedure blank	LP BLK (3)		
Rock standard	LP BHVO-2 (1)		<b>280,9</b>
Rock standard	LP BHVO-2 (2)		<b>299,3</b>
Rock standard	HP BHVO-2 (1)	<b>403,9</b>	
Rock standard	LP BCR-2 (1)		<b>350,5</b>
Rock standard	LP BCR-2 (2)		<b>306,8</b>
Rock standard	LP GSP-2		<b>199,3</b>
Rock standard	HP GSP-2 (1)	<b>1139,4</b>	
Rock standard	HP GSP-2 (2)	<b>850,8</b>	
HP full procedure blank	HP BLK (1)	<i>Not distinguishable from the Hf content of the final dilution acid</i>	
HP full procedure blank	HP BLK (2)		
HP full procedure blank	HP BLK (3)		
	<b>AEGINA</b>		
Skotini and-dac	IA102	<b>133,7</b>	
Enclave Skotini and-dac	IA101		<b>190,6</b>
Bt-hbl-dac Palaiochora	HP IA61	<b>341,0</b>	
Bt-hbl-dac Palaiochora	LP IA61		<b>172,0</b>
Bt-hbl-dac Megali Korifi	HP IA59	<b>248,6</b>	
Bt-hbl-dac Megali Korifi	LP IA59		<b>135,3</b>
Enclave bt-hbl-dac M. K.	IA66	<b>147,5</b>	
Bt-hbl-dac Kokinovrahos	HP IA56	<b>249,5</b>	
Bt-hbl-dac Kokinovrahos	LP IA56		<b>130,1</b>
Bt-hbl-dac Kokinovrahos	IA346	<b>184,0</b>	
Enclave bt-hbl-dac Kokk.	HP IA338	<b>304,7</b>	
Enclave bt-hbl-dac Kokk.	LP IA338		<b>120,8</b>
Enclave bt-hbl-dac Kokk.	HP IA338 (2)	<b>155,7</b>	
Enclave bt-hbl-dac Kokk.	IA348		<b>183,1</b>
Bt-hbl-dac Tourli	IA65	<b>187,6</b>	
Enclave bt-hbl-dac Tourli	IA104	<b>148,8</b>	
Bt-hbl-dac Koutalou	IA327	<b>244,7</b>	
Enclave bt-hbl-dac Kout.	IA321		<b>273,1</b>
Kakoperato rhyodac	HP IA97	<b>280,3</b>	
Kakoperato rhyodac	LP IA97		<b>8,2</b>
Enclave Kakoperato	IA98		<b>209,7</b>
Hbl-And Nikolaki	IA73		<b>192,5</b>
Oros bas-and (young)	IA83		<b>221,0</b>
Enclave bas-and Oros	IA72		<b>232,5</b>
Oros andesiet	IA80		<b>200,4</b>
Hy-andesiet Oros	IA75		<b>213,3</b>
Enclave hyp-and Oros	IA77		<b>225,7</b>
Enclave hyp-and Oros	IA77 (2)		<b>196,6</b>

Sample information		Hf isolated at VUA (ng)	
		HP digestion	LP digestion
	<b>METHANA</b>		
volk ( $\delta 1$ ) (>0.9Ma)	IM313	<b>297,3</b>	
volk ( $\delta 1$ ) (>0.9Ma)	IM313		<b>110,5</b>
$\beta\alpha 2$ - Malisa bas-and	IM364		<b>193,3</b>
Q $\delta$ k2 - pumice	IM383	<b>216,8</b>	
$\alpha 2$ - Paleo Kastro	IM379	<b>219,6</b>	
$\alpha 2$ - Enclave	IM373		<b>251,3</b>
xenolith $\alpha 2$	IM376A	<b>170,6</b>	
xenolith $\alpha 2$	IM376B	<b>162,5</b>	
Loutses SE	DPM8	<b>236,7</b>	
Enclave Loutses SE	DPM9	<b>211,4</b>	
Loutses S	DPM28	<b>244,1</b>	
Loutses S	DPM28		<b>163,5</b>
Enclave Loutses S	DPM29A	<b>159,1</b>	
Enclave Loutses SW	DPM32	<b>181,6</b>	
Loutses SW	DPM33	<b>211,8</b>	
Loutses NW	DPM66	<b>191,5</b>	
Tsonaka	DPM42	<b>300,5</b>	
Tsonaka	DPM42		<b>157,0</b>
Enclave Tsonaka	DPM56B		<b>333,5</b>
Kossona Vouno	DPM34	<b>247,9</b>	
Enclave K.Vouno	DPM36		<b>193,7</b>
Enclave K. Vouno	DPM41A		<b>185,4</b>
$\alpha 3$	IM319		<b>190,1</b>
$\alpha 3$ - Enclave	IM318		<b>253,8</b>
$\delta 6$	IM295		<b>200,6</b>
$\delta 6$ - Enclave	IM294		<b>195,4</b>
$\alpha 6$	IM315		<b>200,8</b>
$\alpha 6$ - Enclave	IM316		<b>217,4</b>
$\alpha 8$ -	IM303		<b>253,3</b>
$\alpha 8$ - Enclave	IM301		<b>160,4</b>
xenolith in q $\delta$ k2	IM386	<b>36,9</b>	
xenolith in $\pi\tau\kappa\beta\alpha 8$	IM394	<b>59,0</b>	
$\beta\alpha 8$ Mavri Petra	IM36	<b>253,5</b>	
$\beta\alpha 8$ Mavri Petra	IM36		<b>183,0</b>
$\alpha\delta 8$ Mavri Petra	IM29	<b>306,1</b>	
$\alpha\delta 8$ Mavri Petra	IM29		<b>164,4</b>
$\alpha\delta 8$ - enclave	IM400		<b>224,9</b>
	<b>POROS</b>		
'Andesite'	IP46	<b>207,8</b>	
'Dacite'	HP IP49	<b>251,2</b>	
'Dacite'	LP IP49		<b>123,9</b>
Enclave 'daciet'	IP50		<b>225,1</b>

**Table 1.** Quadrupole ICP-MS obtained data on the Hf amounts isolated and recovered at the VUA Isotope Geochemistry Facility from the 83 volcanic rock samples, standards, blanks and duplicates (indicated by '(2)'). LP = Low Pressure, HP = High Pressure. Grey coloured cells point out the significant difference between the Hf concentration retrieved from LP and HP dissolved aliquots from 11 samples. This is due to incomplete to non-dissolution of zircon during LP digestion, and might reveal isotopic differences between groundmass and zircons of these samples.