# Fractionation processes of platinum-group-elements in natural systems and experiments

By

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Montréal, QC, Canada

October 2022

A thesis submitted to McGill University in partial fulfilment of the requirements for the

degree of Doctor of Philosophy

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 The second row refers to time needed for a measured (real) laurite to grow by diffusion through multiple chromites. The third row matches the second, but accounting for equilibration between chromite rims and interiors.

## LIST OF SUPPLEMENTARY MATERIAL

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## LIST OF ABBREVIATIONS

2D = two dimensional3D =three dimensional 4D =four dimensional AH = after heatingBH = before heating BMS = base-metal-sulfides BSE = back-scatter electronCCD = charge-coupled device CMBR = chromite-melt boundary region EDS = energy dispersive spectroscopy Fiji = Fiji Is Just ImageJ FOV = field of view  $GGG = Gd_3Ga_5O_{12}$ GmbH = Gesellschaft mit beschränkter Haftung (company with limited liability) GSECARS = Geo Soil Enviro Consortium for Advanced Radiation Sources HE = high energyHPHT = high-pressure and high-temperature HTG = high temperature generator INGV = Istituto Nazionale di Geofisica e Vulcanologia LA-ICP-MS = laser ablation inductively coupled mass spectrometry LabMaTer = Laboratoire des matériaux terrestres PGE = platinum-group elements PGM = platinum-group minerals PSI = Paul Scherrer Institut RS = recommended standard

sCMOS = scientific Complementary Metal-Oxide-Semiconductor SEM = scanning electron microscopy sd = standard deviation SR = synchrotron radiation STP = Syrmep Tomo Project SYRMEP = SYnchrotron Radiation for MEdical Physics TOMCAT = TOmographic Microscopy and Coherent rAdiology experimenTs TomoLab = Tomography Laboratory UK = United Kingdom USA = United States of America VGStudio = Volume Graphics Studio vol. % = volume percent wt. % - weight percent  $\mu$ CT = computed microtomography ca. = circa (about)e.g. = exempli gratia (for example) etc. = et cetera (and other similar things)  $ex \ situ = off \ site$ i.e. = id est (that is) *in situ* = in the original place n.b. = nota bene (take notice) *post mortem* = following an event *vs.* = versus (against)

## LIST OF SYMBOLS AND UNITS

$\sim =$ approximately	$\mu A = micro ampere$
° = degree	$\mu$ m = micrometer
$\infty = infinity$	A = ampere
$\times$ = multiplied by	C = Celsius
# = number	GeV = giga electron volt
% = percent	GPa = giga Pascal
+ = plus	h = hour
$\pm = plus/minus$	K = Kelvin
§ = section	keV = kilo electron Volt
0 V any charaction	kV = kilovolt
p = X-ray absorption	m = meter
$\lambda = X$ -ray wavelength	min = minute
$\mu = X$ -ray linear attenuation coefficient $\mu = melt viscosity$	mm = millimeter
	MPa = mega Pascal
$\rho = \text{density}$	ppb = part per billion
$\varphi = \text{porosity}$	ppm – part per million
	ppin – part per minion
g = gravitational acceleration	s = second
h = height	W = watt
$\mathbf{k} = \mathbf{thousand}$	y = year
k = permeability	
N = number	$fO_2 = oxygen fugacity$
Q = flow rate	
w = width	
x = maximum ellipsoid axis	
y = intermediate ellipsoid axis	
z = minimum ellipsoid axis	
Z = atomic number	

## ABSTRACT

This study investigates concentration processes of platinum-group elements (PGE) in natural and synthetic systems. In particular, the formation of PGE micro-nuggets in the laboratory and the formation of the platinum-group mineral (PGM) laurite in nature.

In Chapter 2, I describe the commissioning of a controlled atmosphere induction furnace designed at the third generation synchrotron facility Elettra (Trieste, Italy). The furnace is designed for high resolution *in situ* and *ex situ* studies of materials and geomaterials, using laboratory and synchrotron radiation-based hard X-rays microradiography and computed microtomography. It can operate from 773 to 1723 K with heating and cooling control to within 5 K. The heat is homogeneously distributed within the sample holder where the thermal gradient is less than 5 K over ca. 5 mm. The main advantages of the furnace are demonstrated through several examples of experimental applications that highlight the various processes in geo- and material sciences that can be studied.

In Chapter 3, I use the Elettra induction furnace to study nugget formation by X-ray computed microtomography ( $\mu$ CT). Nuggets are micron to nanometer sized PGE crystals that form either by rapid cooling at the end of a high-pressure and high-temperature (HPHT) experiment or at high-temperature due to change in oxygen fugacity ( $fO_2$ ) during the experiment. The PGE partition, solubility and diffusion are studied through HPHT experiments, and thus it is vital to accurately determine PGE concentration in experimental run products. This is hindered by the formation of PGE micro-nuggets during experiments. PGE micro-nuggets are also present in natural samples, and thus the transport of PGE by nuggets in natural systems is possible, highlighting the necessity of nugget formation studies. I have imposed a fugacity gradient within experimental charges that I melted using the Elettra furnace, and imaged prior and post heating, using X-ray  $\mu$ CT. I have determined the number, relative

size and location of nuggets obtained by three-dimensional (3D) hard X-ray imaging and established that nuggets form at high temperature due to an oxygen fugacity gradient.

In Chapter 4, I study laurites in Stillwater chromitite layers by X-ray µCT in order to accurately measure volumes of all phases and study their textural relationship in three dimensions. Laurite is the main host of Ru in chromitite layers of several major PGE ore deposits and understanding the formation of laurite furthers our knowledge of their genesis. Laurite formation has been an area of much scientific debate with two prevailing formation hypotheses: the formation of laurite by direct crystallization from the melt and the formation of the laurite as a product of chromite entrapment of base-metal-sulfides (BMS). I found that the laurite volumes are sufficient to account for all the Ru in the investigated samples. I have studied laurite formation by assuming the Ru was sourced from the medium in which the laurites are currently found: from the melt for laurites located outside of chromites, and from the chromites for laurites located within them. For laurites located outside of chromite crystals, there was sufficient time and melt volume to allow laurite crystallization directly from the melt. This was possible due to the efficient percolation of Ru-bearing silicate melts through permeable chromite cumulates. For laurites located within chromite crystals, one chromite mineral does not hold sufficient Ru, and several neighboring chromites must supply Ru for a single laurite. Depending on the laurite volume, Ru diffusion through multiple chromites would take between 64 k to 400 k years.

Keywords: platinum-group elements, platinum-group minerals, laurite, nuggets, Stillwater, Ru diffusion, X-ray microtomography, induction furnace, *in situ* imaging, 3D imaging

## RESUMÉ

Cette étude examine les processus de concentration des éléments du groupe du platine (EGP) dans les systèmes naturels et synthétiques. En particulier, la formation de micro-pépites d'EGP en laboratoire et la formation de la laurite, un minérale du groupe du platine (MGP) dans la nature.

Dans le chapitre 2, je décris la mise en service d'un four à induction à atmosphère contrôlée conçu au synchrotron de troisième generation Elettra (Trieste, Italie). Le four est conçu pour des études *in situ* et *ex situ* à haute résolution de matériaux et de géomatériaux, en utilisant la microradiographie à rayons X durs basée sur le rayonnement synchrotron et en laboratoire et la microtomographie informatisée. Il peut fonctionner de 773 à 1723 K avec un contrôle du chauffage et du refroidissement à moins de 5 K. La chaleur est répartie de manière homogène dans le porte-échantillon où le gradient thermique est inférieur à 5 K sur env. 5 millimètres. Les principaux avantages du four sont démontrés à travers plusieurs exemples d'applications expérimentales qui mettent en évidence les différents processus en géosciences et sciences des matériaux qui peuvent être étudiés.

Dans le chapitre 3, j'utilise le four à induction d'Elettra pour étudier la formation de pépites par microtomographie par rayons X ( $\mu$ CT). Les pépites sont des cristaux d'EGP de la taille du micron au nanomètre qui se forment soit par refroidissement rapide à la fin d'une expérience à haute pression et à haute température (HPHT), soit à haute température en raison d'un changement de la fugacité de l'oxygène ( $fO_2$ ) au cours de l'expérience. La partition, la solubilité et la diffusion des EGP sont étudiées par le biais d'expériences HPHT, et il est donc essentiel de déterminer avec précision la concentration d'EGP dans les produits expérimentaux. Ceci est entravé par la formation de micro-pépites d'EGP au cours des expériences. Les micro-pépites d'EGP sont également présentes dans les échantillons naturels, et donc le transport

d'EGP par les pépites dans les systèmes naturels est possible, soulignant la nécessité d'études de formation de pépites. J'ai imposé un gradient de fugacité dans les charges expérimentales que j'ai fondues à l'aide du four d'Elettra, et imagé avant et après le chauffage, à l'aide de rayons X  $\mu$ CT. J'ai déterminé le nombre, la taille relative et l'emplacement des pépites obtenues par imagerie tridimensionnelle (3D) à rayons X durs et j'ai établi que les pépites se forment à haute température en raison d'un gradient de fugacité d'oxygène.

Dans le chapitre 4, j'étudie les laurites dans les couches de chromite de Stillwater par µCT aux rayons X afin de mesurer avec précision les volumes de toutes les phases et d'étudier leur relation texturale en trois dimensions. La laurite est le principal hôte de Ru dans les couches de chromite de plusieurs gisements majeurs de minerai d'EGP et la compréhension de la formation de la laurite approfondit notre connaissance de leur genèse. La formation de laurite a été un domaine de nombreux débats scientifiques avec deux hypothèses de formation dominantes: la formation de laurite par cristallisation directe à partir de la fonte et la formation de la laurite en tant que produit du piégeage de chromite de sulfures de métaux de base (SMB). J'ai trouvé que les volumes de laurite sont suffisants pour rendre compte de tout le Ru dans les échantillons étudiés. J'ai étudié la formation de laurite en supposant que le Ru provenait du milieu dans lequel se trouvent actuellement les laurites: de la fonte pour les laurites situées à l'extérieur des chromites, et des chromites pour les laurites situées à l'intérieur de celles-ci. Pour les laurites situées à l'extérieur des cristaux de chromite, il y avait suffisamment de temps et de volume de fusion pour permettre la cristallisation de la laurite directement à partir de la fusion. Cela a été possible grâce à la percolation efficace des silicates fondus contenant du Ru à travers des cumulats de chromite perméables. Pour les laurites situées dans des cristaux de chromite, un minéral de chromite ne contient pas suffisamment de Ru, et plusieurs chromites voisines doivent fournir du Ru pour une seule laurite. Selon le volume de laurite, la diffusion du Ru à travers plusieurs chromites prendrait entre 64 000 et 400 000 années.

Mots clés: éléments du groupe du platine, minéraux du groupe du platine, laurite, pépites, Stillwater, diffusion de Ru, microtomographie aux rayons X, four à induction, imagerie *in situ*, imagerie 3D

#### DEDICATION

To Pia and Inga, everything I do I for you.

Marko

## ACKNOWLEDGEMENTS

I would like to acknowledge my supervisor Don R. Baker without whom this thesis would not be possible. Don your patience, hard work and expertise have made this thesis a reality and I will forever be grateful for that. You have taught me everything I know about experimental petrology and allowed me to work on a project of my own design. I would also like to thank my co-supervisors Sarah Jane Barnes and Lucia Mancini who have both at a different time taken me in their respective scientific domains, taught me all I know about analytical geochemistry and X-ray tomography, and supported me through this process. You have inspired my scientific interests and I hope I can, in some small way, continue in your footsteps.

I would be remiss if I did not thank William Minarik who served on my advisory committee and helped many times when I needed to discuss scientific problems. I also thank Anthony E. Williams-Jones who served as my internal examiner and Margherita Polacci who served as my external examiner, for taking the time to evaluate my work, and all the members of my thesis defense committee.

I want to thank Dany Savard and Lang Shi who helped with analytical work and Nicola Sodini without whom creating the furnace at Elettra would be impossible. All the staff at Elettra especially Giuliana Tromba, Diego Dreossi, Adriano Contillo have made this not only a reality but a very enjoyable experience. I look forward to working with you in the future.

To Anne Kosowski, Kristy Thornton and the late Angela Di Ninno I owe a debt of gratitude and an acknowledgement in this thesis. They have always been available to help with any problems that may have arisen not to mention brought their light and fun demeanor to the department.

I would like to thank all my coauthors not mentioned previously, Pia Pleše, Nicoletta Marinoni, Lucia Pappalardo, Gabriele Lanzafame, Alessio Veneziano and Mattia Pistone. You have brought your expertise and hard work to each of our manuscripts and made them not only possible but also infinitely better.

I would like to thank my mother Manja and mother-in-law Ester, your constant support and help allowed me to go through this journey and complete this thesis.

I want to thank Catherine, Fiona, Sanja, Tomislav, Lovro, Ste and Longbo. I will always fondly remember your friendship, help and advice. I do not know if I could have finished this thesis without that.

Finally, but most importantly, I want to thank my wife Pia Pleše. You have inspired me to start on this journey, been with me through the highs and the lows, helped with not only your scientific insights, but also your support and love through the toughest times. I could not and would not have done this without you, so this is all for you. You and Inga are everything to me; I begin to pay back all the time I spent away from you and all the sacrifices you have had to make, today.

## CONTRIBUTION TO ORIGINAL KNOWLEDGE AND CONTRIBUTION OF AUTHORS

Chapters 2 to 4 presented in this thesis correspond either to published manuscripts or to manuscripts in preparation for submission to scientific journals. All research presented is original. Chapter 2 was published in the Journal of Synchrotron Radiation and Chapters 3 and 4 have not been previously published elsewhere.

Chapter 2 is titled "A compact and flexible induction furnace for *in situ* X-ray microradiography and computed microtomography at Elettra: design, characterization and first tests" by Marko Kudrna Prašek, Mattia Pistone, Don R. Baker, Nicola Sodini, Nicoletta Marinoni, Gabriele Lanzafame and Lucia Mancini. It was published in the Journal of Synchrotron Radiation. Lucia Mancini, Mattia Pistone, Don R. Baker and Nicola Sodini designed the initial induction furnace. I worked on the optimization and complementary design of the furnace and with the technical support of Nicola Sodini commissioned it for the Elettra synchrotron. I worked on the high-temperature experiments with Lucia Mancini, Nicoletta Marinoni, Mattia Pistone and Gabriele Lanzafame. Don R. Baker provided his expertise in data analysis, interpretation and contributed to the discussion of scientific ideas. All authors contributed to writing the manuscript.

Chapter 2 reports our development of a new and novel high-temperature furnace commissioned at Elettra that is a significant contribution to dynamic systems and sample environmental devices, due to its ease of transport and setup at various radiation sources, versatility of application to the study of natural and synthetic systems, and improved temperature control. The furnace provides the possibility to study sample changes at elevated temperatures with an improved temperature measurement accuracy.

Chapter 3 is titled "Synchrotron X-ray computed microtomography measurements of platinum nuggets in basaltic melt" and is a manuscript in preparation for publication by Marko

Kudrna Prašek, Don R. Baker, Sarah-Jane Barnes, Alessio Veneziano and Lucia Mancini. I performed the high-temperature experiment material preparation, made the polished sections, performed the SEM and LA-ICP-MS analysis and with Lucia Mancini and Alessio Veneziano performed the X-ray imaging of the high-temperature experiments. I performed the data analysis and wrote the manuscript. Sarah-Jane Barnes and Don R. Baker provided their expertise in data analysis, interpretation and contributed to the discussion of scientific ideas. All authors contributed to writing the manuscript.

In chapter 3 we demonstrate the novel approach to Pt nugget formation studies using *in situ* high-temperature experiments imaged with X-ray microtomography. The presence of nuggets in experimental samples influences partitioning and solubility studies, and it is not yet resolved whether they are a high-temperature or quench phenomenon. We found nuggets at varying oxygen fugacity, even oxidizing conditions. We provide evidence Pt nuggets should not be included in partitioning and solubility studies.

Chapter 4 is titled "The formation and incorporation of laurite in chromitite layers of the Stillwater complex – insights from X-ray imaging" and is a manuscript in preparation for publication by Marko Kudrna Prašek, Sarah-Jane Barnes, Don R. Baker, Lucia Mancini, Lucia Pappalardo and Pia Pleše. I performed the X-ray data analysis, made the polished sections, performed the SEM analysis and wrote the manuscript. Sarah-Jane Barnes, Lucia Mancini and Don R. Baker provided their expertise in data analysis, interpretation and contributed to the discussion of scientific ideas. Lucia Pappalardo performed the X-ray scans at the Istituto Nazionale di Geofisica e Vulcanologia, provided her expertise in data analysis, interpretation and contributed to the discussion of scientific ideas. Pia Pleše contributed to the discussion of scientific ideas. All authors contributed to writing the manuscript.

In chapter 4 we used X-ray microtomography and mathematical modeling to provide insight into the formation of laurite and chromitite layers of the Stillwater complex. We found the laurites are larger than previously found by two dimensional studies and used this data to test multiple laurite formation hypotheses. We show that although laurite formation by either Ru diffusion through chromite minerals or by crystallization from the melt is possible, the former is more probable and in chapter 5 suggest possible approaches to further investigate the laurite formation. Page intentionally left blank

## **CHAPTER 1**

## Introduction

#### **1.1.General introduction**

The platinum-group elements (PGE) are essential to many aspects of everyday life, although they might not be at the forefront of the public's eye. The group consists of (in alphabetical order): iridium (Ir), osmium (Os), palladium (Pd), platinum (Pt), rhodium (Rh) and ruthenium (Ru). PGE are critical metals with a wide range of uses, from medical treatments and advanced electronics to catalytic converters in automobiles (Zientek and Loferski, 2014; Johnson Matthey, 2020). Ru, Re and Os are used in the manufacturing of electrical contacts and Ru is a vital component in solar cells (Harvey and Day, 2016). In geochemistry and cosmochemistry, PGE (along with Au and Re) are vital as tracers of nucleosynthetic sources, the formation of the Solar System, early planetary accretion and differentiation, core formation, mantle-core, and mantle-crust interactions (Harvey and Day, 2016). They are used to study volcanism, the formation of various ore deposits, ocean circulation, weathering, and biogeochemical cycling (Harvey and Day, 2016). Due to the current and projected need for PGE (Johnson Matthey, 2020) it is important to understand the mineral hosts, mineral associations, and mechanisms involved in their transport and deposition.

The PGE are defined by chemists as the triads Ru, Rh, Pd, and Os, Ir, Pt, which behave in a similar manner (Cotton and Wilkinson, 1988). In the Earth's crust and mantle they fractionate from each other, with the Ir-group (IPGE: Os, Ir, Ru) behaving in a compatible manner and having higher melting temperatures, and with the Pt-group (PPGE: Pt, Pd, Rh) having lower melting temperatures. Platinum and palladium are more incompatible (Barnes et al., 1985), while rhodium behaves in an intermediate fashion. PGE have a strong preference for the metallic phase, but in the absence of metals, at the  $fS_2$  and  $fO_2$  conditions in the Earth's crust, they are highly chalcophile ( $D_{sulfide/silicate} = 10^3 - 10^6$ ; Fleet et al., 1993; Roy-Barman et al., 1998; Ballhaus et al., 2006; Mungall and Brenan, 2014).

PGE fractionation can in part be explained by the crystallization of a Fe-Ni-Cu sulfide (base-metal-sulfide, BMS) liquid. During crystallization of a BMS liquid, IPGE and Rh partition into the first mineral to crystallize, monosulfide solid solution, and Pt and Pd concentrate in the fractionated BMS liquid. However, even in the absence of BMS, the PGE are still fractionated. In particular, chromite rich rocks are rich in IPGE (e.g., Prichard et al., 2017) and in evolved rocks Pd is enriched over Pt (e.g., Skaergaard: Andersen et al., 1998).

Various processes have been proposed for the fractionation of PGE. One of the most commonly suggested is that IPGE are less soluble than Pd and Pt, and Pt in turn is less soluble than Pd (Ertel et al., 1999; Blaine et al., 2005; Borisov, 2005; Laurenz et al., 2013). Thus, a magma may become saturated in IPGE minerals early in its crystallization history and early formed cumulates are enriched in IPGE (e.g., von Gruenewaldt et al., 1986; Scoon and Teigler, 1994; Oberthür, 2002; Zientek et al., 2002; Naldrett et al., 2009). In intrusive rocks platinum-group minerals (PGM) rich in IPGE, in particular laurite, Ru(Os,Ir)S<sub>2</sub>, are commonly present and are interpreted to be the product of this saturation. As crystallization continues, and provided that the magma does not become saturated in BMS liquid, the magma may also become saturated in FePt and thus fractionate Pd from Pt in evolved magmas. However, experimental work has also shown that IPGE partition into spinel (Righter et al., 2004; Brenan et al., 2012; Wijbrans et al., 2015) and olivine (Righter et al., 2004; Brenan et al., 2005) and thus the fractionation of IPGE from Pt and Pd could be due to simple crystal fraction or retention of these elements during partial melting. In the latter case, post cumulus processes are necessary to form the laurite observed in chromite rich rocks.

#### 1.2. Thesis outline

In this thesis, I examined the various processes that could fractionate the PGE. First by considering the experimental work used to estimate the concentrations of PGE required to bring about saturation of a magma. These experiments have been plagued by the formation of nano-to micrometer sized PGE particles (nuggets) in the glass of the experiments (Brenan et al., 2016 and references therein). The timing of nugget formation during experiments. i.e., whether nuggets are a quench or saturation phenomenon, is critical to the question of whether magmas can become saturated in IPGE or Pt, and remains unresolved. In order to study the nugget formation timing, nugget formation was observed *in situ* in three-dimensions. This is an entirely novel approach to the study of nugget formation, which allows the investigation of the sample volume with a non-destructive approach. To do so, I was involved in the commissioning and testing of an induction furnace at the third generation Elettra synchrotron radiation facility in Basovizza (Trieste, Italy) (Chapter 2).

Using the Elettra furnace, experiments with Pt showed that the nuggets represent saturation at levels of Pt present in magmas and nuggets are not quench phenomena, but are instead formed due to an imposed oxygen fugacity gradient (Chapter 3).

Secondly, I investigated the problem of IPGE fractionation in chromitites on samples from the Stillwater Complex. Stillwater was chosen as it is one of the three main layered mafic intrusion PGE deposits, and I had access to a well-documented sample set (Prichard et al., 2017). Understanding the formation of laurite is complex because laurite is found in cumulus rocks. Laurite crystallization is possible, but the complexity of post cumulus processes makes the results ambiguous. Thus, three-dimensional imaging is needed to understand the true laurite size and distribution (Chapter 4). I conducted textural investigations in three dimensions using laboratory-based X-ray computed microtomography ( $\mu$ CT) to obtain accurate volumes and locations of all phases, and I used this information to apply mass balance and diffusion calculations.

In Chapter 2, titled "A compact and flexible induction furnace for *in situ* X-ray microradiograhy and computed microtomography at Elettra: design, characterization and first tests", I present the technical aspects of an induction furnace newly developed at the third generation Elettra synchrotron to operate at the SYRMEP beamline and TomoLab laboratory of Elettra. My goal was to utilize the furnace to obtain *in situ* and real time 3D data on the nugget formation timing, but the furnace had to first be commissioned and tested, before I could proceed.

In Chapter 3, titled "Synchrotron X-ray computed microtomography measurements of platinum nuggets in basaltic melt", I present the 3D imaging results on nugget formation during high-temperature experiments performed with the Elettra induction furnace. I investigated the hypothesis that nugget formation is governed by either  $fO_2$  change during the experiment or temperature variation during quench. By using the novel approach of 3D imaging in this application, I show that nuggets formed in the part of the sample that underwent  $fO_2$  change.

In Chapter 4, titled "The formation and incorporation of laurite in chromitite layers of the Stillwater complex – insights from X-ray imaging", I studied the formation of laurite  $(Ru,Os,Ir)S_2$  via X-ray  $\mu$ CT applied to chromitite layers of the Stillwater Complex. I obtained accurate volume measurements and locations of all phases in samples. Combining my findings with previously established geochemical data and performing mass balance and diffusion calculations, I examined the viability of several proposed laurite formation processes. The textural relationship between chromites and laurites (i.e., the location of one relative to the other) was central to both the calculations and assessment of different formation models.

In Chapter 5, the concluding chapter, I summarize my results and conclusions from Chapters 2 - 4.

#### **1.3.** Literature review

#### 1.3.1. The nugget effect on PGE studies

The geochemical behavior of PGE is modelled upon experimentally obtained partition coefficients between sulfide and silicate liquids. These are, however, extremely variable and through the years have been reported as ranging from  $10^3 - 10^6$  (e.g., Crocket et al., 1992; Fleet et al., 1999) and greater than  $10^7$  (Pruseth and Palme, 2004; Fonseca et al., 2011). The latter values have been questioned (e.g., Laurenz et al., 2013), but recent attempts to determine partition coefficients have not significantly narrowed the range of values (e.g., Mungall and Brenan, 2014). Some of these variations may be due to different melt compositions used in the experiments, as well as different experimental conditions (e.g., temperature, pressure, oxygen fugacity).

Partition coefficients, PGE saturation, and diffusion experiments are complicated by the presence of nuggets. Nuggets are extremely small (nm to µm scale) PGE metals present in silicate and sulfide melts. Anenburg and Mavrogenes (2016) showed how nuggets may form within silicate melts, and later coarsen and combine into PGM, providing a mechanism of PGM formation that does not necessitate a sulfide melt. González-Jiménez et al. (2019) confirmed the presence of Pt nanoparticles in metasomatic silicates and sulfides from Patagonian mantle xenoliths, but the presence of very small PGE particles and or small PGM in natural samples has been long recognized (e.g., Augé, 1986; Augé et al., 1998; Park et al., 2012; Wirth et al., 2013; Junge et al., 2014; Kamenetsky et al., 2015; Arguin et al., 2016).

Nuggets are important because their presence and analytical treatment lead to the wide range of reported PGE partitioning values. If one chooses to include nuggets in the analysis, i.e., take the entire glass composition as representative, nuggets will increase the measured PGE compositions in the glass, leading to an apparent higher PGE solubility and providing lower calculated partition coefficients. Conversely, one may choose to completely exclude nuggets from PGE concentration calculations. Several studies have done the latter (e.g., Ertel et al., 2001, 2006; Laurenz et al., 2013), but this means blindly assuming all nuggets were stable in the experiment at high pressures and temperatures, which need not be true (Brenan et al., 2016). Thus, an attempt to assess the origin of nuggets must be performed in PGE partitioning and solubility studies.

The initial goal was to study the formation of nuggets through *in situ* and real time observations using X-rayimaging. Directly observing, in near real time, the moment of nugget formation, whilst controlling the environmental parameters of the experiment (temperature, oxygen fugacity) would provide a definitive resolution of the nugget formation timing. Towards that goal, a dedicated induction furnace was commissioned and tested at the Elettra synchrotron. Unfortunately, due to unforeseen movement of bubbles and nuggets during imaging (the movement was faster than the temporal resolution of the scan), the obtained real time information is obscured. Thus, only prior and post heating *in situ* scans are used in the presented nugget study.

I investigated the nugget effect by heating previously prepared starting material at a dedicated furnace available at the Elettra synchrotron radiation laboratory in Basovizza (Trieste, Italy) and recording the evolution of the system in the 3D domain using X-ray  $\mu$ CT. I tested the hypothesis that a change in oxygen fugacity within the sample would prompt nugget precipitation. The experimental results show that nuggets formed in the part of the sample that underwent a change in oxygen fugacity, thus confirming the model proposed by Bennet et al. (2014). The obtained results also show that to verify a nugget-free experiment, high-resolution X-ray  $\mu$ CT is an essential technique because nuggets can be missed if they are not homogeneously distributed throughout the sample. Additionally, the uneven 3D distribution of
the nuggets along with the quench rate of the Elettra furnace imply that it is unlikely the nuggets formed during quench.

## 1.3.2. PGE enrichment of chromitite layers in layered mafic intrusion PGE deposits

PGE occur in many different rock types; layered mafic intrusions (LMI), ophiolites, subcontinental lithospheric mantle peridotites, Uralian-Alaskan-Aldan complexes, and placer deposits (see review in O'Driscoll and González-Jiménez, 2016). The economically most significant PGE concentrations are located in a few LMI-associated PGE deposits. Foremost among them are three LMI with stratiform chromitite deposits (Naldrett, 2011; Zientek, 2012; O'Driscoll and González-Jiménez, 2016): the Bushveld Complex (Republic of South Africa), the Stillwater Complex (Montana, USA), and the Great Dyke (Zimbabwe).

The minerals hosting PGE in chromitites are chromite, base-metal-sulfides (BMS) and platinum-group minerals (PGM). Chromitites in the three foremost intrusions mentioned previously, and in some ophiolites (e.g., chromitites of Shetland Ophiolite, Prichard and Lord, 1993) are (I)PGE-enriched, relative to the magmas from which they are though to crystallize (von Gruenewaldt et al., 1986; Scoon and Teigler, 1994; Oberthür, 2002; Zientek et al., 2002; Naldrett et al., 2009).

The geochemical behavior of PGE is controlled by their sulfide-silicate partitioning and the melting and crystallization of BMS (e.g., Morgan, 1986; Handler and Bennett, 1999; Lorand et al., 1999; Luguet et al., 2003; Pearson et al., 2004; Rohrbach et al., 2007). The main BMS hosts of PGE are pyrrhotite,  $Fe_{1-x}S$ , and pentlandite (Fe,Ni)<sub>9</sub>S<sub>8</sub> (Cabri, 1992; Alard et al., 2002; Lorand et al., 2008). However, the LMI chromitites are S-poor (< 100 ppm; Barnes et al., 2009) and contain few BMS (Prichard et al., 2017) and the sparseness of BMS within chromite-rich layers of the three main LMI-associated PGE deposits suggests an introduction of PGE through a sulfide liquid cannot adequately explain the PGE-enrichment of the chromitites (Barnes et al., 2009). The next important (I)PGE host is chromite ( $Fe^{2+}Cr^{3+}{}_{2}O_{4}$ ). Chromite does not host all PGE, as most PPGE (Pd, Pt) are incompatible in chromite (Brugmann et al., 1987; Barnes and Picard, 1993; Puchtel and Humayun, 2001; Pitcher et al., 2009; Day, 2013). Contrastingly, the IPGE (Ru, Os, Ir) and Rh are compatible (Capobianco and Drake, 1990; Righter et al., 2004), as Ru<sup>3+</sup> and Rh<sup>3+</sup> are thought to substitute for Cr<sup>3+</sup> in the chromite structure (Brenan et al., 2016). Experimentally determined partition coefficients of IPGE and Rh into chromite range from 40 – 200, at a *f*O<sub>2</sub> around Ni-NiO (NNO) and up to ~ 1000 at higher *f*O<sub>2</sub> 's (Righter et al., 2004; Brenan et al., 2012).

Laurite is the main Ru, Os and Ir host in chromitites (Prichard et al., 2004; Godel et al., 2007; Junge et al. 2014; Barnes et al., 2016), and thus laurite formation is investigated to resolve the IPGE enrichment of chromitites. Laurite occurs in several textural locations; within chromite minerals (Brenan et al., 2016 and references therein), interstitial to chromite minerals (Barnes et al., 2016; Prichard et al., 2017; Wavrant, 2017), close to BMS (e.g., Prichard et al., 2004), at BMS margins (e.g., Cawthorn et al., 2002), which are in turn located at either chromite mineral margins or chromite triple junctions (e.g., Junge et al., 2014), and at chromitesulfide-silicate triple junctions (3D data from Godel et al., 2010). However, the mechanisms responsible for laurite formation remain poorly understood. Currently, there are three main proposed models. The first model proposes laurite crystallization from a silicate melt (Hiemstra, 1979; Legendre and Augé, 1986; Merkle, 1992; Peck et al., 1992; Augé et al., 1998; Prichard et al., 1994; Brenan and Andrews, 2001; Andrews and Brenan, 2002; Zaccarini et al., 2002; Bockrath et al., 2004). The second model also proposes laurite crystallization from a silicate melt, but at the chromite-melt interface due to a local decrease in fO<sub>2</sub> (Finnigan et al., 2008). In both models, some laurites could become incorporated into chromite crystals whilst these grow and envelop laurites. The third model proposes a diffusive exchange of elements between IPGE-rich chromites and the BMS sintered between them, which converts the latter to laurite (Barnes et al., 2016). The fourth model proposes laurite formation after hydrous melting of a sulfide-bearing norite (Mathez, 1995; Boudreau and Meurer, 1999; Veksler and Hou, 2020). For all proposed IPGE enrichment models, the location of laurite in relation to chromites and BMS is used to deduce enrichment processes.

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## CHAPTER 2

# A compact and flexible induction furnace for *in situ* X-ray microradiography and computed microtomography at Elettra: design, characterization and first tests

# 2.1. Rationale

In Chapter 1, the challenges raised by the presence of PGE nuggets in experimental charges and the fractionation of (I)PGE in (ultra)mafic melts was briefly presented. I first focus on the nugget issue. As the timing of nugget formation is at the center of the nugget issue, I wanted to observe their formation *in* (almost) real time, *in situ*, and under high temperature, by applying a nondestructive method of 3D imaging. However, in order to perform such experiments a furnace had to be commissioned and tested.

In Chapter 2 I present the commissioning of a dedicated induction furnace operating under controlled atmosphere conditions. The furnace is located at the Elettra synchrotron radiation laboratory in Basovizza (Trieste, Italy). The furnace has been successfully commissioned and tested, and is currently in active use at Elettra. To showcase the range of the furnace's capabilities, I present several examples of X-ray imaging experiments performed at high temperatures.

The following chapter was published in the Journal of Synchrotron Radiation as Kudrna Prašek, M., Pistone, M, Baker, D.R., Sodini, N., Marinoni, N., Lanzafame, G. and Mancini, L. (2018). A compact and flexible induction furnace for *in situ* X-ray microradiograhy and computed microtomography at Elettra: design, characterization and first tests. Journal of Synchrotron Radiation, 25, 1172-1181. DOI: <u>https://doi.org/10.1107/S1600577518005970</u>. Reproduced with permission from the publisher.

#### 2.2. Abstract

A compact and versatile induction furnace for *in situ* high-resolution synchrotron and laboratory hard X-ray microradiography and computed microtomography is described. The furnace can operate from 773 to 1723 K. Its programmable controller enables the user to specify multiple heating and cooling ramp rates as well as variable dwell times at fixed temperatures allowing precise control of heating and cooling rates to within 5 K. The instrument can work under a controlled atmosphere. Thanks to the circular geometry of the induction coils, the heat is homogeneously distributed in the internal volume of the graphite cell (ca. 150 mm<sup>3</sup>) where the sample holder is located. The thermal gradient within the furnace is less than 5 K over a height of ca. 5 mm. This new furnace design is well suited to the study of melting and solidification processes in geomaterials, ceramics and several metallic alloys, allowing fast heating (tested up to 6.5 K s<sup>-1</sup>) and quenching (up to 21 K s<sup>-1</sup>) in order to freeze the sample microstructure and chemistry under high-temperature conditions. The sample can be held at high temperatures for several hours, which is essential to follow phenomena with relatively slow dynamics, such as crystallization processes in geomaterials. The utility of the furnace is demonstrated through a few examples of experimental applications performed at the Elettra synchrotron laboratory (Trieste, Italy).

Keywords: X-ray microtomography; *in situ* synchrotron X-ray imaging; induction furnace; metals; volcanic rocks; ceramics.

#### **2.3. Introduction**

The physical and chemical behaviour of materials such as metals, ceramic alloys and geomaterials at high-temperature and/or high-pressure conditions was traditionally analysed in the quenched final run products at room-temperature conditions after synthesis. The development of certain materials such as foams, compacts in liquid-phase sintering and ceramics requires inherently dynamic processes and full understanding of the processes that generate the materials (i.e., through chemical analysis, mechanical testing, thermal treatment, chemical reactions, etc.). As a result of analytical limitations, our understanding of these dynamic processes is almost exclusively based upon *ex situ* analyses of the final products rather than analyses of the systems during such processes. The optical opacity of many materials (both natural and artificial) makes observations in visible light difficult, if not impossible. Therefore, these observations usually have to be performed on thin sections of the sample after the dynamic process is finished or has been interrupted by quenching. Although this procedure has led to many important insights and improvements in the materials that we use, this 'snapshot' sampling can provide at most only an incomplete view of spatially and temporally variable systems. Many phenomena still remain unclear because it has been impossible to observe and record the formation processes continuously.

The high-penetrating power of hard X-rays and the advent of new instruments and novel imaging techniques has made microradiography (Miller and Beech, 1972; Curreri and Kaukler, 1996; Sen et al., 1997; Li et al., 2006; Rack et al., 2009) and computed microtomography (µCT) (Mayo et al., 2012; Fife et al., 2012; Riesch et al., 2013; Maire and Withers, 2014; Bouttes et al., 2015; De Schryver et al., 2016) unique tools to observe internal structures of materials undergoing processes such as melting, vesiculation, and the growth, dissolution or reaction of crystalline phases. Two-dimensional and three-dimensional X-ray imaging experiments carried

out under controlled high-temperature conditions represent the next generation of *in situ* timeresolved experimental observations of materials and the processes forming them.

Recently, advancements in technology such as sCMOS detectors, coupled with both fast-response scintillator screens and new X-ray sources, e.g., synchrotron sources producing high-brillance radiation, have stimulated renewed interest in time-resolved investigations (Fife et al., 2012; Daudin et al., 2015; Mokso et al., 2010; 2017; Yu et al., 2017; Zhao et al., 2017). Also, the advent of new laboratory systems able to perform fast microradiography and  $\mu$ CT experiments (Larsson et al., 2011; De Schryver et al., 2016) paved the way for the application of these techniques to novel *in situ* and real-time studies. The design of an instrument able to perform this kind of study has to be carefully tailored to the technical features of the X-ray imaging system employed.

In earlier experiments, magmatic and volcanic applications have been investigated by synchrotron-based X-ray imaging at high temperatures. The first experiments (Bai et al., 2008) were carried out on the GSECARS beamline in a custom furnace at the Advanced Photon Source of Argonne National Laboratory (USA). An accurate temperature control was obtained by using a Pt–Rh/Pt thermocouple. The employed furnace was well suited for *in situ* X-ray radiography and for *ex situ*  $\mu$ CT studies. More recently, *in situ*  $\mu$ CT experiments were carried out at the TOMCAT beamline of the Swiss Light Source (PSI, Villigen, Switzerland) using a laser furnace system (Fife et al., 2012; Baker et al., 2012; Pistone et al., 2015a,b). This instrument allowed rapid sample heating and the acquisition of ultrafast tomographic scans on a scale of 1 s or even faster (Baker et al., 2012). The furnace temperature was measured with an optical pyrometer that could not monitor an eventual thermal gradient within the sample holder. Both of these furnaces could operate at temperatures higher than 1500 K in air (i.e. under non-controlled atmosphere conditions), and using either alumina or boron nitride sample holders, the latter characterized by a high thermal conductivity (20 – 60 W m<sup>-1</sup> K<sup>-1</sup>).

Although these experiments expanded our understanding of dynamic processes at high temperatures, we saw the need for a different furnace design. An important feature of a high-temperature furnace is the ability to work under a controlled atmosphere (Boller et al., 2017), essential when investigating, for instance, samples containing elements with multiple oxidation states (e.g., Fe, Mn, V, S). Moreover, when operating in air, the boron nitride sample holders might oxidize and degrade, especially at temperatures above 1573 K (Lavrenko and Alexeev, 1986). A potential issue in the design of a furnace is the size of the hot spot with respect to the sample dimensions. A limited size hot spot can potentially induce thermal gradients both laterally (between sample and holder) and vertically (along the sample). Finally, an accurate monitoring of thermal fluctuations and gradients is an essential requirement.

In this contribution, we present the design and fabrication of a compact and flexible high-temperature induction furnace system for the *in situ* study of high-temperature processes using both hard X-ray microradiography and  $\mu$ CT techniques. The furnace can work under a controlled atmosphere and can be used to melt geomaterials, ceramics and many metallic alloys at temperatures from 773 to 1723 K.

An accurate control of heating and cooling rates can be achieved and used for material melting (with a heating rate up to 6.5 K s<sup>-1</sup> as tested so far) and solidification (with a cooling rate up to 21 K s<sup>-1</sup>, to freeze the sample microstructure and chemistry under high-temperature conditions).

This new furnace has been designed and optimized to operate at the SYRMEP beamline of the Elettra synchrotron facility in Basovizza (Trieste, Italy). This beamline is characterized by a photon flux that limits the use of ultrafast hard X-ray  $\mu$ CT (Tromba et al., 2010). Therefore, the furnace has been conceived to investigate dynamic processes characterized by relatively slow kinetics, with microtomographic scan durations on a scale of 60–180 s and microradiography studies on the scale of 0.1 – 0.5 s (at the 2.4 GeV mode of the Elettra machine). However, the instrument could be also installed in another hard X-ray  $\mu$ CT beamline with a more brilliant source or even in an open conventional X-ray  $\mu$ CT scanner.

Here, we also provide a few examples to demonstrate the utility and flexibility of this new furnace design.

#### 2.4. Furnace design and calibration

At Elettra, two different facilities are available for hard X-ray imaging: the SYRMEP beamline based on a bending magnet source, and the TomoLab instrument, a custom-developed  $\mu$ CT instrument equipped with a sealed microfocus X-ray source (Polacci et al., 2009; Zandomeneghi et al., 2010). The furnace design was optimized to use the available photon flux, maximum vertical size of the X-ray beam and energy range of the SYRMEP beamline. However, the furnace also can be easily installed in the TomoLab station in order to carry out laboratory-based X-ray microradiography and  $\mu$ CT experiments.

In §§2.4.1 and 2.4.2 the main technical features of the two X-ray facilities at Elettra are described, and in §§2.4.3 and 2.4.4 the furnace design and the temperature calibration procedure are detailed.

## 2.4.1. The SYRMEP beamline setup

Two different configurations at the SYRMEP beamline (<u>http://www.elettra.eu/elettra-beamlines/syrmep.html</u>) are compatible with the new induction furnace. In the first configuration, a highly coherent and nearly-parallel X-ray beam is delivered by a bending magnet source. The beam has a laminar shape with a maximum size of 220 mm (h) by 6 mm (w). The energy of the X-ray beam is tuned to the sample material through a double-crystal Si(111) monochromator between 8.3 and 40 keV. The sample is located at ca. 24 m from the X-ray source. Sample projections are typically recorded over a total scan angle of 180° by a

CCD camera coupled to a Gadox scintillator screen by a fiber optic taper. In the second configuration, X-ray  $\mu$ CT experiments are carried out in white-beam mode. The sample is located at ca. 16 m from the source and the maximum beam size at the sample is 160 mm (h)  $\times 4$  mm (w). In this configuration, images are acquired using a microscope system based on a 16-bit, 2048  $\times$  2048 pixel, water-cooled sCMOS detector coupled with a 17 mm-thick LSO:Tb scintillator screen. The X-ray beam is filtered ('pink beam') to select a mean energy in the X-ray spectrum optimized for the specific sample of interest. Using polychromatic radiation allows higher photon flux and thus decreases the scan duration of  $\mu$ CT experiments. Furthermore, such a setup is ideal for the sCMOS detector, which has the capability to acquire and read out individual projections at rates that are orders of magnitude faster than the traditional CCD cameras. For both configurations, experiments were performed in propagation-based phase-contrast mode (Cloetens et al., 1997; Polacci et al., 2010).

When performing dynamic  $\mu$ CT experiments a compromise between the number of projections, exposure time per projection and final image quality is needed. The selection of these parameters is strongly affected by the type of sample (material, microstructure, texture) and on the specific physical properties we wish to investigate. At SYRMEP, using a mean energy of 24 keV, it has been possible to obtain a 'good' image quality with an exposure time per projection of the order of 0.2 s (at the 2.4 GeV mode of the Elettra machine) producing a scan duration of 180 s if 900 projections are acquired. The scan duration can be reduced if a weakly absorbing sample is investigated under high-temperature conditions and the mean energy is set in a range of 10–15 keV (highest flux region), or by reducing the number of projections per scan. At present, the setup is mechanically limited by the maximum speed of the rotation stage to a minimum acquisition time for a full three-dimensional data set acquisition of 35 s. In July 2018 a new airbearing rotation stage will be installed at SYRMEP that will remove this limitation.

#### 2.4.2. The TomoLab instrument setup

The TomoLab station complements the SYRMEP beamline in terms of energy range and (http://www.elettra.eu/lightsources/labs-andvertical beam size services/tomolab/tomolab.html). The X-ray source can operate in a voltage range from 40 to 130 kV, with a maximum current of 300 µA and a minimum focal spot of 5 mm. The mostused detector is a 12-bit, water-cooled,  $4008 \times 2672$  pixel CCD camera consisting of a fullframe CCD imager coupled to a Gadox scintillator by a fiber-optic taper. The effective pixel size of the detector is 12.5 mm  $\times$  12.5 mm corresponding to a maximum field of view of 50 mm (h)  $\times$  33 mm (w). Exploiting the magnification effect offered by the cone-beam geometry (Feldkamp et al., 1984), the source-to-sample and source-to-detector distances can be varied over a range of ca. 1.5 m in order to achieve a spatial resolution close to the focal spot size of the source and to work both in absorption and propagation-based phase-contrast mode (Wilkins et al., 1996; Zandomeneghi et al., 2010). Being an open instrument, different types of detectors can be easily installed.

#### 2.4.3. Furnace design

The furnace developed at Elettra for synchrotron X-ray  $\mu$ CT imaging is based on the principle of the Oersted effect: an electrically conducting object can be heated by electromagnetic induction through heat generated in the object by the application of a radiofrequency signal (Brown et al., 1947). An important feature of the induction heating process is that the heat is generated inside the object itself, instead of by an external heat source. Thus, samples can be heated or solidified very rapidly; the process is easily controlled and there is no need for external electrical contacts.



**Figure 2.1. (a)** A schematic view of the furnace assembly. This does not show the upper hollow zirconia rod holding the thermocouple used for monitoring the temperature during experiments. The quartz glass tube channels the nitrogen gas injected into the bottom of the furnace and is used to prevent oxidation of the graphite susceptor at high temperatures. The X-ray beam passes through the target location to be imaged (i.e., sample in the graphite susceptor) without encountering the induction coils (in red). The curvilinear black arrows indicate the rotating part of the setup during X-ray tomographic experiments (induction coils are fixed). (b) The custom-designed (at Elettra) sample holder that allows continuous sample rotation while the gas delivery system is stationary.

Figure 2.1(a) schematically shows the design of the Elettra furnace, which is composed of the heating element, the graphite cylindrical shell containing the sample holder or crucible, two zirconia rods directly connected to the upper and lower end of the graphite shell, and a quartz tube surrounding the graphite shell and the zirconia rods. The heating element of the furnace is an induction coil controlled by a HTG-1200/0.45 N high-frequency generator produced by Linn High Therm GmbH company (Germany). The cylindrical geometry of the coil ensures uniform distribution of heat around the sample. Moreover, the choice of a vertical arrangement of the coil generates a large hot spot for the sample and is compatible with the geometry of a CT experiment. The coil shape has been customized in order to keep a 6 mm-high region 'coil-free' and a uniform hot spot (< 5 K variation) within the internal volume of the graphite shell traversed by the X-ray beam.

In addition to the desired flexibility in controlled rates of heating, cooling and temperature gradient, an important requirement is that the furnace interferes as little as possible with the X-ray path, which is essential for  $\mu$ CT experiments. Indeed, X-rays should pass through a sample and reach the detector with a minimum attenuation caused by the furnace. Graphite was chosen as the susceptor for the furnace because of its low X-ray absorption coefficient. With the different materials selected for the furnace construction, the X-ray transmission is ca. 67 % at an energy of 24 keV in the absence of a crucible.

For the experiments reported in this contribution, we used an alumina crucible with an internal diameter of 3.9 mm and an internal vertical size of 7 mm. This material was selected for its chemical and thermal stability as well as its reasonable transmission of X-rays at energies above 20 keV (the crucible has an X-ray transmission of about 62 % at 24 keV). Alumina also has a moderate thermal conductivity (5.43 W m<sup>-1</sup> K<sup>-1</sup> at 1673 K) ensuring heat transfer to the sample, and can be reliably used up to temperatures of 1873 K. Other materials such as boron nitride (ca. 94 % of X-ray transmission at 24 keV) could be selected for the crucible depending

on the specific scientific application and temperature. The alumina crucible, zirconia rods and graphite shell were manufactured by the INTELLION company (France).

The quartz tube surrounding the graphite shell and the zirconia rods allows a continuous flux of nitrogen gas that minimizes the amount of ambient air around the graphite components of the furnace to prevent the oxidation of the graphite susceptor at high temperatures. In principle, different gases and/or gas mixtures can be injected in the quartz tube allowing observations in a controlled atmosphere. In order to investigate the possibility of controlling the oxygen fugacity ( $fO_2$ ) in the furnace, glasses of basaltic composition [48.89 wt. % SiO<sub>2</sub> and a total iron oxide (FeO + Fe<sub>2</sub>O<sub>3</sub>) concentration of 10.57 wt. %] were fused at 1573 K for 4 h. If the oxygen fugacity in the furnace is controlled by oxidation of the graphite susceptor to carbon monoxide, then ferric and ferrous iron in the melt will be reduced to form Fe metal and the sample will become magnetic; but after the experiment the sample was not magnetic. Although we have no direct measurement of the oxygen fugacity, this test is consistent with an estimated oxygen fugacity of  $10^{-3}$  for a melt in the presence of N<sub>2</sub> gas flowing through the furnace (Nafziger et al., 1971). This test indicates the possibility of controlling the  $fO_2$  by traditional mixing of gases such as CO<sub>2</sub>–CO or CO<sub>2</sub>–H<sub>2</sub> (Nafziger et al., 1971). For example, at 1273 K we should be able to vary the oxygen fugacity in the furnace from  $10^{-18}$  to  $10^{-6}$  by using differing mixtures of CO<sub>2</sub> and CO (Deines et al., 1974). A more detailed study focused on oxygen fugacity control in the furnace will be performed in the near future.

A metallic support, designed and manufactured at Elettra, holds the quartz tube and the zirconia rod at the base of the furnace and allows the gas injection (see Fig. 2.1b). This support can be directly screwed into the centre of the high-resolution rotation stage of the  $\mu$ CT apparatus on both the SYRMEP beamline and the TomoLab station. The hot spot is approximately 140 mm above the rotation stage ensuring that temperature-sensitive micromechanical parts are kept at room temperature.

Figure 2.2 shows the furnace in operation installed in the experimental hutch of the SYRMEP beamline. During experiments, the power supply and the furnace are set inside the X-ray hutch. The instrument is interfaced to the computer allowing the remote control of the furnace *via* an RS-232 communication port. Customized control software for maintaining the temperature of interest as well as controlling the rates of heating and cooling is currently under development at Elettra.



**Figure 2.2.** Image showing an overview of the experimental setup used with the induction furnace in operation for *in situ* measurements as installed at the SYRMEP beamline of Elettra.

#### **2.4.4.** Temperature control and calibration

Temperature control is performed by increasing or decreasing the amperage (power) of the high-frequency generator either manually or via the software control. Before the experiments, the furnace is heated to the desired temperature levels with the S-type Pt–Rh/Pt thermocouple positioned vertically inside the crucible instead of the sample (in contact with its internal base) and in the same location. The temperature values were measured by using a FLUKE 54 II temperature controller. The temperature is measured for the corresponding amperage in order to build a calibration curve similar to the one in Figure 2.3, which is then used during real experiments to control the temperature by varying the amperage.

For *in situ*  $\mu$ CT experiments, a continuous sample rotation over 360° is required and thus the quartz tube and all of the components it surrounds rotate during X-ray image acquisition as well. Plastic tubes used for N<sub>2</sub> flow into the quartz tube are connected to the metallic support described above (Fig. 2.1b). The support in Figure 2.1(b) allows continuous rotation of the sample while the connected gas inlet and outlet tubes remain stationary. The thermocouple is removed during sample rotation; however, temperature calibration is conducted prior to and after each experimental run or when any furnace component is replaced or modified. The calibration procedure prior to *in situ* experiments is always conducted with the X-ray beam illuminating the furnace. It is essential to take into account furnace heating by the beam itself, especially when working in white or pink beam mode.



**Figure 2.3.** (a) A selection of radiographic images and (b) the corresponding temperature calibration curve at ambient pressure using materials with known melting points: Borax (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>; 1020 K; green diamonds) and Au (1337 K; red triangles). Empty blue circles and empty orange squares indicate temperature readings during two different calibrations at the SYRMEP beamline. Temperature uncertainty is  $\pm$  5 K and is the size of the symbols.

A temperature calibration prior to experiments was also performed by melting standard materials with known melting points. The first calibration experiment was performed on the SYRMEP beamline in monochromatic beam mode using anhydrous Borax (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>; melting point at 1020 K) and gold foil (melting point at 1337 K). The phase transition from solid to liquid of each material was monitored using *in situ* X-ray microradiography. Images were acquired by a watercooled, 12-bit, 4008 × 2672 pixel CCD camera under the following conditions: energy = 24 keV, sample-to-detector distance = 350 mm, exposure time per projection = 3 s (2.0 GeV mode at Elettra), binning = 2 × 2, effective pixel size = 9.0 mm.

A selection of radiographic images and the corresponding calibration curve are shown in Figures 2.3(a) and 2.3(b), respectively: the first calibration (blue circles) was performed from 773 to 1673 K; the second calibration (orange squares) was performed to check for temperature hysteresis between different heating and cooling cycles. Both calibrations are in good agreement with an uncertainty of  $\pm$  5 K at the melting points of Borax and Au, respectively. A movie containing the full radiographic sequence during a calibration is reported in the supporting information (see Movie S2.1).

Temperature calibration using standard materials was also performed by *in situ* X-ray microradiography in the TomoLab station. In addition to Borax and Au foil, a cube-shaped Cu sample (melting point at 1358 K) was used. The melting of each material was monitored using *in situ* X-ray microradiography under the following conditions: source-to-sample distance = 260 mm, source-to-detector distance = 600 mm, voltage = 70 kV, current = 113 mA, filter = 0.5 mm Al, exposure time per projection = 4 s, binning =  $5 \times 5$  and effective pixel size = 27.2 mm. A selection of radiographic images and the corresponding calibration curve are shown in Figures S2.1(a) and S2.1(b) of the supporting information, respectively. There is a movie containing the full radiographic sequence during a calibration reported in the supporting information (see Movie S2.2).

A calibration test was also conducted *ex situ*, when the furnace was not installed on the rotation stage, using two S-type thermocouples (both connected to the FLUKE 54 II controller) and a different support setup. A top thermocouple was inserted into the sample holder, the second was placed within the hollow zirconia rod at the base of the sample holder. The distance between the two thermocouples was ca. 3 mm. The aim of this test was to determine the thermal gradient within the crucible by measuring the temperature difference between the top and bottom thermocouples and the real temperature of the sample contained in the crucible. Some fluctuations of the calibration curves were observed caused by a loose contact between the thermocouple bead and the base of the crucible. The geometry of the graphite cell (Fig. 2.1a), and therefore the heating, is different from the centre of the cell where the crucible is located and where the magnetic field is designed to be homogeneous. In order to circumvent this problem we repeated the calibration, moving the crucible vertically (ca. 5 mm) with only one thermocouple inserted. Combining the results of both procedures, a thermal gradient within the crucible of less than 5 K over a height of ca. 5 mm was estimated.

#### **2.5. Experiments**

We selected two representative samples from the fields of material and Earth sciences in order to demonstrate the applicability of the furnace and unravel the dynamic processes that lead to the formation of sample textures. Specifically, vesiculation and crystallization processes in synthetic rocks and ceramic samples were investigated by *in situ* two-dimensional and threedimensional X-ray imaging. An *ex situ* experiment on the synthetic rock sample was also performed.

## 2.5.1 Sample description and preparation

The ceramic material (sample CD1) investigated was a mixture of clay minerals, feldspar and quartz. This composition represents the foundation of much of the traditional ceramic technology (Carty and Senapati, 1998). In particular, clays provide plasticity to the green body and are dominated by kaolinite with a lower amount of smectite, montmorillonite, illite, quartz and an organic fraction (Standard Definition of Terms Related to Ceramic Whitewares and Related Products, 1996). Feldspar acts as a flux, promoting fusion of the raw materials upon heating, whereas quartz plays the role of a filler, which generally constitutes the coarsest particles in a green body and prevents fired ceramic bodies from shrinking, warping and sagging (Marinoni et al., 2011). In this preliminary study, our attention is focused on pore growth during the firing process of a ceramic body. Distribution, size and type of pores/voids are key features affecting ceramic durability in terms of chemical and physical resistance (Bernasconi et al., 2012, 2014).

A parallelepiped-shaped sample (section of ca. 2.5 mm  $\times$  2.5 mm and ca. 3 mm in height) was cut out from a larger specimen and inserted in the alumina crucible.

A synthetic rock (sample F60) was prepared from previously melted hydrous (4.2 wt. % H<sub>2</sub>O) dacite glass mixed with an aliquot of 60 vol. % quartz crystals (average size = 68 mm), simulating crystal-rich volcanic rocks. Sample preparation, synthesis and characterization of such a material are described in detail by Pistone et al. (2017). Two cylindrical samples (F60a and F60b), each with a diameter of ca. 2.6 mm and height of ca. 3 mm, were prepared. Each sample was mounted in an alumina crucible.

## 2.5.2 Experimental protocol for the ceramic sample CD1

Sintering of sample CD1 was explored using the phase-contrast  $\mu$ CT setup configuration in white beam mode at SYRMEP. Six  $\mu$ CT scans were recorded, one at room temperature, four during heating of the sample at 923, 1273, 1473 and 1513 K [using heating

increments of 10 A at each step following the calibration curve reported in Fig. 2.3(b)], and a final one after quenching to room temperature (switching off the temperature controller). At each high-temperature step, the temperature was kept constant for 10 min [except for the last step (1513 K), where the temperature was kept constant for 2 min] in order to initiate the chemo-physical process and allow the sample to reach textural stability; after this time the  $\mu$ CT scan was performed. This procedure avoids acquisition during highly dynamic phase transitions and sample movement that could have led to blurred X-ray images. For each  $\mu$ CT scan, a set of 1000 projections was acquired over an angular range of 180°. The exposure time per projection was 0.5 s (2.4 GeV mode of Elettra) and the total duration of each  $\mu$ CT scan was 500 s. An effective pixel size of 2.4 mm was set for the sCMOS detector placed at 200 mm from the sample.

The software suite Syrmep Tomo Project (STP; Brun et al., 2015; 2017) was used to reconstruct two-dimensional axial slices from the sample projections applying the filtered back projection algorithm (Herman, 1980; Kak and Slaney, 1988). Before image reconstruction, a single-distance phase retrieval algorithm was applied to the projection images (Paganin et al., 2002) using the STP software and setting the  $\delta/\beta$  ratio to 70.

#### 2.5.3. Experimental protocol for the synthetic rock sample F60

Sample F60a was investigated using the white-beam configuration available at SYRMEP for phase-contrast microradiography and  $\mu$ CT experiments. The X-ray beam was filtered by 1.5 mm of Si + 1.0 mm of Al, corresponding to a spectrum with a mean X-ray energy of ca. 25 keV. The sample-to-detector distance was set to 200 mm; with these conditions, low-noise individual sample projections with 2.4 mm pixel edge-lengths were captured in 2 s at the 2.0 GeV mode of Elettra.

The vesiculation of the sample at different temperatures (1073, 1373 and 1673 K) was achieved using incremental heating [10 A per step following the calibration curve in Fig.

2.3(b)]. As experiments were carried out at room pressure, heating these hydrous samples synthesized at 68 MPa triggered water exsolution and bubble formation (Pistone et al., 2017). The sample was held at each temperature step for a time interval of 2 min and at the maximum temperature for 10 min before quenching. During the different stages of sample heating and quenching, sequences of *in situ* X-ray microradiographs were acquired.

Additionally, at each quenched step from the specified temperature a  $\mu$ CT scan (a set of 900 projections over an angular scan of 180°, scan duration 30 min) was recorded 10 min after quenching. The Paganin algorithm with a constant  $\delta/\beta$  ratio equal to 80 was applied prior to the reconstruction by using the STP software.

Sample F60b was investigated by *in situ* microradiography and *ex situ*  $\mu$ CT experiments at the TomoLab station following the same temperature ramps described for sample F60a, and following the calibration curve in Fig. S2.1(a) of the supporting information. In particular, *ex situ*  $\mu$ CT scans were acquired with identical thermal histories to those on SYRMEP, but after each high temperature ramp followed by quenching it was necessary to dismount the crucible containing the sample from the furnace and install it on the rotation stage in the TomoLab. The following  $\mu$ CT conditions were used for the scans: voltage = 50 kV, current = 160 mA, filter = 0.25 mm Al, exposure time per projection = 7 s, total scan duration = 3.5 h). In combination with the 2 × 2 binning applied to the CCD camera pixels, the source–sample and source–detector distances were set to 80 and 400 mm, respectively, in order to acquire images at an effective pixel size of 5 mm; 1800 tomographic projections were acquired with the commercial software COBRA (Exxim, USA). Ring artefacts in the reconstructed slices were reduced with an algorithm custom-implemented in the Pore3D software library (Brun et al., 2010).

#### 2.6. Results and discussion of the investigated samples

In this section, the main results obtained for the three samples described in §2.5. will be reported and illustrated through both two-dimensional images and three-dimensional views of the samples. For all samples, the two-dimensional images (microradiographs and reconstructed slices) were visualized in the freeware Fiji (Schindelin et al., 2012) while the commercial software VGStudio MAX 2.0 (Volume Graphics, Germany) was employed for the volume renderings.

## 2.6.1. Results on the ceramic sample CD1

In Figure 2.4, a reconstructed two-dimensional axial slice of sample CD1 prior to heating is displayed together with a zoomed region of interest (outlined by the yellow rectangle). The green body consists of feldspar and angular quartz crystals randomly distributed in a clay matrix mainly composed of kaolinite and illite. The clay fractions occasionally agglomerate leading to visible rounded aggregates. Figures 2.5(a) and 2.5(d) provide, respectively, a volume rendering of the whole sample within the crucible and the pore distribution in a selected volume of interest ( $300 \times 300 \times 300$  voxel space) prior to heating, extracted by the *Pore3D* software after a three-dimensional automatic Otsu thresholding. The pores are a few micrometres in size and are randomly dispersed in the matrix and/or at the boundary between crystals and matrix; they are interpreted as air bubbles entrapped during sample preparation. A total porosity of ca. 0.5 vol. % was computed.



**Figure 2.4.** Reconstructed axial slices (left column) and a selected region of interest corresponding to the yellow rectangle (right column) of sample CD1 after experiments performed at room temperature before heating, during heating at 1373 K and 1473 K, and at room temperature after quenching from 1513 K. Arrows indicate features representative of textural changes.



**Figure 2.5.** Three-dimensional renderings of sample CD1 at room temperature before heating, at 1473 K, and at room temperature after quenching from 1513 K; panels (a), (b) and (c) show the whole sample within the crucible; in panels (d), (e) and (f) the segmented pore phase (in yellow) in a selected volume of interest  $(300 \times 300 \times 300 \text{ voxel space})$  is represented.
At 923 K, although the total porosity of the sample is still quite similar to that of the non-heated sample, we observed the development of interconnected pores that can be attributed to the dehydroxylation reactions of kaolinite and lead to a more global porous structure. On the other hand, a limited expansion of the whole sample is observed and can be attributed to several phenomena such as loss of adsorbed water, allotropic transformation of  $\alpha$  to  $\beta$  quartz, etc. Note that such a transformation induces a volume increase of about 2 % (Singer and Singer, 1963; Celik, 2010).

At 1373 K, melting of the clay fraction begins with the formation of a liquid phase, as highlighted in Figure 2.4, where the rounded clay aggregates apparently dissolve away. Conversely, no relevant reaction takes place involving filler and flux components which maintain their original microstructure (grain size and shape). The appearance of a liquid phase induces a shrinkage of the sample and a decrease of the total porosity. In particular, the smallest pores disappear whereas the largest still remain as isolated structures in the resulting ceramic.

At 1473 K, quartz and feldspar crystals disappear (see Fig. 2.4) because they melt and the amount of the liquid phase increases. This phase penetrates the pores, closing and isolating even the largest pores. A shrinkage of the sample of ~ 8 % was measured (Fig. 2.5b) with a total porosity of ~ 1.6 vol. %. In Figure 2.5(e), a volume rendering of the pore distribution is shown. The same is observed at 1513 K, where the original interconnected porosity evolves into a more compact matrix containing isolated and closed spherical pores of  $15 - 20 \,\mu\text{m}$  in diameter which can be attributed to overfiring conditions.

After firing, the ceramic body appears as a dense structure, which results from a sequence of intracrystalline (regarding a single crystalline/amorphous phase) and intercrystalline (involving more than one crystalline/amorphous phase) reactions (Gualtieri, 2007).

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Focusing our attention on the ceramic microstructure after quenching from 1513 K, a porosity of ~ 3 vol. % was determined and is characterized by spherical pores, which are a few micrometres in size and are mostly isolated (see Figs. 2.4 and 2.5f). A few microcracks around the quartz crystals are also observed. The final ceramic shrinkage is ~ 10 % (Fig. 2.5c).

The results presented highlight the power of the *in situ* experiments for exploring the firing process of ceramic materials. In particular, the possibility of following the growth/development of pores in real time, which play a key role in the technological performance of a ceramic body, as well as the appearance of the melt fraction upon heating, provides fundamental information for the optimization of the ceramic firing process.

#### 2.6.2. Results on the synthetic rock sample F60

A region of interest selected from two-dimensional axial slices in the central part of sample F60a after quenching at different temperatures is shown in Figure 2.6; the corresponding three-dimensional renderings, cropped from the analysed volumes as in Figure 2.6, are displayed in Figure 2.7. The *in situ* experiments captured a multistage sequence of vesiculation and outgassing that natural magmas may experience during their rise and eruption prior to fragmentation: nucleation and growth of bubbles from room temperature (Figs. 2.6a, 2.7a) up to 1073 K (Figs. 4.6b, 4.7b); volume inflation and initial bubble coalescence in the temperature range of 1073–1373 K (Figs. 2.6c, 2.7c); and bubble coalescence and outgassing leading to sample contraction from 1373 to 1673 K (Figs. 2.6d, 2.7d).



**Figure 2.6.** Region of interest selected from reconstructed axial slices of sample F60a after *in situ* X-ray  $\mu$ CT experiments performed at SYRMEP: (a) at room temperature before heating, and at room temperature after quenching at (b) 1073 K, (c) 1373 K and (d) 1673 K. The sample was kept at the selected temperature for 10 min and then quenched by switching off the furnace.



**Figure 2.7.** Volume renderings corresponding to cropped analyzed volumes of sample F60a at the same temperatures reported in Figure 4.6 and for the same crop of the investigated sample volume.

A similar behaviour was observed in sample F60b at lower spatial resolution and with much longer scanning times (see details in §2.5.3) during *ex situ* conventional X-ray  $\mu$ CT experiments performed at the TomoLab station of Elettra (Fig. S2.2 of the supporting information).

These results are suggestive of how the viscosity of the silicic melt surrounding gas bubbles decreases with temperature (e.g., Giordano et al., 2008), and how such a viscosity decrease strongly controls the different stages of dynamic vesiculation textures, ranging from frothy bubbles (1073 K) to tubular structures made by connected bubbles (1373 K), and finally to large coalesced bubbles suspended in the crystal-bearing melt (1673 K). These *in situ* and real-time experiments demonstrate the powerful approach of observing dynamic processes that volcanologists could only infer from postmortem microstructures and chemistry of already erupted volcanic samples. Indeed, the vesiculation dynamics of a volcanic sample has been captured with three consecutive sequences of radiographs collected during heating of sample F60a (see Movie S2.3 of the supporting information).

# 2.7. Conclusions

We introduce a compact and versatile induction furnace design for both *ex situ* and *in situ* time-resolved experiments at high temperatures (up to 1723 K) using synchrotron and laboratory X-ray microradiography and microtomography. The furnace is specifically designed for applications in the fields of material and Earth sciences and its technical features were optimized for use at the SYRMEP beamline of Elettra in white beam mode. For this reason, and due to the photon flux presently available at the beamline, the induction furnace was designed to provide the necessary thermal conditions for high spatial resolution (1 to 3  $\mu$ m) microtomographic analysis of dynamic processes compatible with total scan durations consistent with relatively slow phase transformations (e.g., melting and crystallization) and

dynamic transport processes at high temperature. Faster processes such as vesiculation in volcanic rocks and foaming of other materials can also be investigated using the same approach reported in this contribution.

The small size and high flexibility of the induction furnace allows its installation at other synchrotron beamlines or its use in an open instrument based on a microfocus X-ray source, such as the TomoLab station of Elettra. This ability will aid in the preparation of synchrotron-based experiments in terms of experimental parameters for image acquisition (X-ray energy, detector pixel size, sample-to-detector distance), temperature triggering for phenomena under study, and to establish convenient temperature ramps for the material of interest. This could be done by microradiography experiments or *ex situ* microtomographic experiments performed at different stages of the high-temperature treatment after quenching of the sample. Finally, *in situ* microtomographic experiments at lower spatial resolution could be also performed for a 'coarse' monitoring of the high-temperature treatments before synchrotron-based experiments at higher contrast and spatial resolution.

This novel high-temperature design opens up new frontiers of *in situ* characterization of materials and the processes forming them. Preliminary experiments performed on synthetic rocks and ceramic samples, exploring the abovementioned possibilities, show that most of the features of interest can be resolved and captured.

#### 2.8. Acknowledgements

The authors are grateful to: B. Cordonnier (Nationaal Archief of the Netherlands), D. Dreossi (Elettra, Italy), F. Arzilli, M. Polacci (University of Manchester, UK) and the Linn High Therm GmbH staff (Germany) for useful discussions during the induction furnace design stage; M. Bregant (INTELLION, France) for support in the choice of materials for the furnace shell and sample holders; the Elettra staff for technical support during the commissioning phase of the instrument; A. G. Whittington (University of Missouri, Columbia, USA) for assisting MP during calorimetric measurements of the synthetic volcanic glass used in this study. The authors appreciated the editorial handling of the manuscript and the valuable comments received during the review process that helped to improve the paper.

# **2.9. Funding information**

MP acknowledges the support of the Ambizione Fellowship of the Swiss National Science Foundation (PZ00P2-168166/1). Portions of this research were funded by a Discovery Grant from the Natural Sciences and Engineering Research Council of Canada (to DRB).

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# 2.11. Supplementary material



Borax - Gold - Copper calibration



**Supplementary figure S2.1.** (a) A selection of radiographic images and (b) the corresponding temperature calibration curve at ambient pressure using materials with known melting points: Borax (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>; 1020 K; green diamonds), Au (1337 K; red triangles) and Cu (1358 K, red squares). Empty blue circles and empty orange squares indicate temperature readings during two different calibrations at the TomoLab station. Temperature uncertainty is  $\pm$  5 K and is the size of the symbols.



**Supplementary figure S2.2.** Supplementary figure showing reconstructed axial slices of sample *F60b* after *ex situ*  $\mu$ CT experiments performed in the TomoLab station: a) at room temperature before heating, and at room temperature after quenching at b) 1073 K, c) 1373 K and d) 1673 K. The sample was kept at each temperature for 10 minutes and then quenched by switching off the furnace.

**Supplementary movie S2.1.** Supplementary movie showing a sequence of *in situ* X-ray microradiographs acquired at the SYRMEP beamline during temperature calibration (see details in section 2.2.4).

**Supplementary movie S2.2.** Supplementary movie showing a sequence of *in situ* X-ray microradiographs acquired at the TomoLab station during temperature calibration (see details in section 2.2.4).

**Supplementary movie S2.3.** Supplementary movie representing concatenated sequences of *in situ* X-ray microradiographs acquired at the SYRMEP beamline for sample *F60a* during each phase of sample heating and quenching following the temperature ramps detailed in section 2.3.3.

All supplementary movies are available for viewing at:

https://scripts.iucr.org/cgi-bin/paper?ay5511

# Afterword to Chapter 2

In the time since Chapter 2 was published as a paper (2018) many new furnaces for use at synchrotrons have been developed. This afterword provides a brief summary of the developments on dynamic systems and sample environmental devices at various synchrotron radiation facilities.

Synchrotron light sources coupled with technological advancement in detector performance have increased the spatial and contrast resolution in imaging experiments and considerably shortened the exposure time (from tens of minutes to seconds, and below). The combined use of stable, accurate and fast rotation stages, increased recording speed, and computer hardware capable of heavy-duty image acquisition, storage and processing, paved the way to ultrafast imaging capabilities and the possibility to record a complete scan at spatial resolutions  $\sim 1 \ \mu m$  in a single second or less (Buffière and Baruchel, 2015; Marone et al., 2020). These advancements in X-ray mCT made it possible to record and observe, in real time (i.e., with a time resolution of  $\leq 1$  s), dynamic process occurring within a geological sample submitted to thermal treatment (e.g., Baker et al., 2012, Pleše et al., 2018). The imaging method associated with the use of environmental sample devices installed on rotation stages, and for in situ and real time experiments, are thus referred to as 4D CT (3D + time) experiments. In situ experiments are recording images at different steps of the sample evolution, freezing a given sample status and recording scans in static conditions (sample not, or only slowly, evolving during the CT scan acquisition). If the environmental conditions are applied to the sample outside the tomographic set up and then the sample is analyzed by a mCT scan, we speak about ex situ microtomographic experiments.

The drive behind pushing the limits of *in situ* experiments is plain; if we are able to monitor changes in 3D and real time, while mimicking natural conditions to the best of current

technological capabilities, can shed light on mechanisms behind hypothesized (but previously unobserved) dynamics and enhance our understanding of natural process governing them (Mancini et al., 2020).

During a technically challenging in situ experiment several prerequisites must be met to ensure success: I) the application of experimental conditions (e.g., temperature, pressure, strain, etc.) that initiate a dynamic process, II) an X-ray transparent sample holder (e.g., graphite, quartz, soft ceramic, boron nitride) to allow the sample to be imaged with X-rays minimizing the holder impact, and III) that the scanning speed exceeds the speed of the process we are trying to record, i.e., adequate time resolution still governs the types of dynamics we can record. The first in situ X-ray CT experiments date to the 1990s' (Guvenilir et al., 1997) and have continued to expand in their application range, scanning speed and spatial resolution. In situ devices might be divided to dedicated furnaces, i.e., devices focused on heating samples, mechanical testing devices (e.g., changing load, tension, torque) and multi-focused devices, where a combination of different parameters are varied (e.g., temperature and pressure). Several devices are translatable to different beamlines or laboratory systems or easily adapted For instance, the RoToPEc (Rotational Tomographic Paris Edinburgh cell) to them. compression and shear capable furnace (Philippe et al., 2016) can be used at both the European Synchrotron Radiation Facility (ESRF) and Diamond beamlines, while the "XRheo" lowtorque rheometric apparatus (Di Genova et al., 2016; Dobson et al., 2020) can be combined with both the Swiss Light Source (SLS) laser powered furnace (Fife et al., 2012) and the commercial Pele furnace at Diamond (Dobson et al., 2020).

Currently there are several *in situ* high-temperature devices designed for specific hard X-ray imaging beamlines. They have their own advantages and limitations based on the furnace design and intended use. Dobson et al. (2020) provides a list of recent *in situ* synchrotron X-ray mCT experiments with real-time resolution, with a specific focus on issues pertinent in

volcanology, e.g., gas bubbles in silicate melts (Baker et al., 2012b, 2019; Colombier et al., 2018; Pleše et al., 2018), melt segregation (Pistone et al., 2015), crystallization (Polacci et al., 2018; Arzilli et al., 2019) and ash particle welding (Wadsworth et al., 2019). Here follows a review of the furnaces available for geological applications at several light sources in approximately the last two decades, with a brief mention of their purpose and design.

#### European Synchrotron Radiation Facility

At ESRF, in situ devices that applied tension or compression were developed already about twenty years ago (Buffière et al., 1999), and several furnaces followed soon after. Bellet et al. (2003) presented a small, resistor-heated furnace able to heat samples up to 1025 °C, with the temperature measured via thermocouples positioned close to the sample. Another device for testing tensile creep under load used resistive heating coils and reported a 36.7 °C mm<sup>-1</sup> temperature gradient in the sample's center (Sket et al., 2008). There were also dedicated furnaces equipped with X-ray transparent windows that used lamps or resistors for heating (Buffière et al., 2010). ESRF continued to develop multi-focused devices, with a tension/compression furnace heated by an induction copper coil that could reach 1500°C (Buffière et al., 2010) and a furnace mounted on a motorized translation apparatus (Billia et al., 2010). A new resistive furnace was introduced in 2015, with reported experiments up to ~ 570 °C (Daudin et al., 2015). In 2016, ESRF introduced the RoToPEc device, capable of simultaneously heating, compressing, and shearing samples during in situ experiments (Philippe et al., 2016). The device can accommodate large samples and generate temperatures up to 2225 °C and pressures up to 15 GPa. The press was designed to fit not only beamlines at ESRF but also those at the Diamond Light Source, and others. Finally, in 2017, a new furnace operating between 400 to 1000 °C was introduced (Boller et al., 2017).

#### Advanced Photon Source

APS has long focused on high-pressure microtomography experiments. Wang et al. (2005) presented a compression apparatus capable of inducing shear strain by twisting the two opposing anvils; the machine could generate pressures up to 8 GPa but had no heating elements at the time. A graphite furnace was later added to introduce the high-temperature aspect and shear deformation experiments were reported with samples at 6 GPa and 525 °C (Wang et al., 2011). The temperature could be sustained at  $\pm$  15 %, but was not directly measured; a thermocouple was inserted in one of the anvils and temperature was calibrated against power consumption, the latter of which was monitored (Wang et al., 2011). A dedicated furnace was also developed, heated by two coils, where the temperature gradients up to ~ 25 °C cm<sup>-1</sup> (Li et al., 2006). In 2008, a ceramic furnace for *in situ* degassing experiments was used to heat silicate glasses at up to temperatures of 1321 °C (Bai et al., 2008). The temperature was measured using a previously calibrated thermocouple, positioned outside of the furnace, and a 5 °C variation in the hot spot was reported (Bai et al., 2008).

#### Swiss Light Source

At SLS, a dedicated furnace can heat samples using two Class 4 diode lasers; its temperature range is from ambient to 1200 °C, and the temperature is measured with non-contact infrared pyrometers (Fife et al., 2012). The furnace's main applications are presented in Marone et al. (2020), with the main limitation being high thermal gradients outside the laser spot (Dobson et al., 2020) when working at temperatures greater than 350 °C.

#### Advanced Light Source

The ALS developed a high-pressure and high-temperature device that could subject a sample to tension or compression while maintaining a maximum temperature of 1750 °C (Bale et al., 2012). Heating was accomplished using six halogen lamps that generated a spherical hot zone of 5 mm, within which the temperature variation was 150 °C; both the temperature and its variations were estimated through lamp calibrations with thermocouples translated across the field of view (Bale et al., 2012). The device was slightly modified shortly after, to obtain temperatures up to 2300 °C, to adjust the hot spot zone by repositioning the halogen lamps and to increase the tension or compression forces (Haboub et al., 2014). Subsequently, the device was rendered capable of testing load-induced sample changes through acoustic emission and of testing flexures imposed through three and four-point bending, but with no temperature-related device changes (Barnard et al., 2017).

#### Diamond Light Source

At the Diamond Light Source, Kareh et al. (2012) combined a shear and compression apparatus with a 1000 °C furnace (providing sparse furnace details). Subsequently, a high temperature cell was established, able to heat samples to above 1300 °C and cool them slowly  $(0.1 °C s^{-1})$  with a thermal precision of  $\pm 0.5 °C$  (Azeem et al., 2017). The cell's heating element is MoSi<sub>2</sub> and the temperature is measured via an outside-furnace placed thermocouple (Azeem et al., 2017). Both previous apparatuses were mainly envisioned for the study of metallic alloy behavior, but Polacci et al. (2018) used the latter furnace to study *in situ* crystallization within silicate melts. Soon after, Diamond implemented a commercially fabricated furnace, the Pele furnace, with the aim of combining it with the XRheo rheometric apparatus (Dobson et al., 2020). The Pele furnace operates from 200 °C to 1250 °C, providing a relatively large hot zone of 20 mm within which the temperature variation is 2 °C and the thermal stability is  $\pm 2 °C$  (Dobson et al., 2020). The temperature is measured using thermocouples inserted close to the sample.

This brief summary of experimental furnaces for synchrotron applications demonstrates their rapid advance in the past 20 years. In the forthcoming years new, and better, furnaces will no doubt be designed that will enhance our experimental capabilities and allow us to investigate new problems.

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# Chapter 3

# Synchrotron X-ray computed microtomography measurements of platinum nuggets in basaltic melt

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#### 3.1. Rationale

In Chapter 3, I apply the previously described Elettra furnace to the nugget issue and study the nugget formation by propagation-based, phase contrast high-resolution X-ray computed microtomography. Such a 3D nondestructive approach has not to date been applied to the study of nuggets. The goal was to observe, in almost real time, the moment of nugget formation, all the while controlling the temperature and oxygen fugacity applied to the sample. This would provide a definitive answer as to whether nuggets are a stable or quench phenomena and improve the determination of PGE concentration in experimental run products.

Using the furnace, I heated previously synthesized starting material, and imaged changes in the sample volumes by using propagation-based, phase-contrast synchrotron X-ray microtomography at the third generation Elettra facility. I investigated whether nugget formation is governed by either temperature variation during quench or oxygen fugacity change during the experiment. The results suggest the latter.

This chapter is being prepared for publication with M. Kudrna Prašek as a first author, in collaboration with Don R. Baker, Sarah-Jane Barnes, Alessio Veneziano and Lucia Mancini.

#### **3.2.** Abstract

Understanding the formation of platinum group element (PGE) deposits is critical for the growing need of these metal resources in the near- and long-term future. Knowledge of partition coefficients, solubilities and diffusion is vital in PGE research, but has been hampered by the formation of micron to nanometer sized PGE crystals (or nuggets) in experimental run products (Brenan et al., 2016). Similar particles have been found in natural systems as well (e.g., Prichard et al., 1981; Park et al., 2012; Wirth et al., 2013; Junge et al., 2014; Kamenetsky et al., 2015; Arguin et al., 2016; González-Jiménez et al., 2019). Nuggets in experimental charges are formed by either changes in oxygen fugacity during the experiment or during rapid cooling (quenching) at the end of the experiment. We have employed a newly commissioned induction furnace at the third generation Elettra synchrotron SYRMEP beamline, described in detail in Kudrna Prašek et al., (2018), to study the platinum (Pt) nuggets using phase-contrast synchrotron X-ray computed microtomography. Here we report results from scans performed on twelve samples before and after heating at temperatures from 1400 to 1250 °C to which an oxygen fugacity gradient has been applied. Platinum nuggets have been identified in all experimental charges before heating in oxidizing conditions and after heating in a more reducing part of the sample. Our results show an increase in nugget number at the reducing part of the sample, but the results are not consistent through all temperatures and heating durations. The nugget number is small and variable (from 5 to 77) in the sample suite and can be easily missed if volumetric characterization techniques are not employed. The preferred nugget distribution close to the meniscus, and the short quenching time in our experiments, leads to the conclusion that nuggets (detectable by 3D X-ray imaging) are not formed during the quenching process. Nuggets we are unable to detect, due to their sub-micron size, could have been formed during quench, but due to the short duration of the quench, their size is

limited to the sub-micrometer scale and thus will have at most a limited impact on analyses used to determine partition, solubility, or diffusion coefficients.

Keywords: nuggets, platinum group elements, in situ imaging, X-ray microtomography

#### **3.3. Introduction**

Understanding the formation of PGE (platinum group elements: Pt, Pd, Rh, Ru, Os and Ir) deposits is vital to the ever-increasing need for PGE in the modern technological society (Johnson Matthey, 2020). Constraining the characteristics of a magma capable of producing a PGE deposit is difficult to achieve without experimentally obtaining information on PGE partitioning and solubility. To illustrate, if we know the partition coefficients of PGE from a silicate magma to a sulfide liquid, and the sulfide liquid later crystalizes into PGE-bearing sulfide minerals, we can estimate the efficiency of ore forming processes. Knowing the solubility of PGE in the silicate liquid gives us an estimate of how much PGE the silicate liquid can hold and transport.

A long-standing challenge in studies of PGE behavior is that in experimental charges, i.e., in silicate melts (which we later analyze as glass), the PGE tend to form PGE or PGE-alloy nuggets, but it is not clear at which point during the experiment they form, in equilibrium at high temperatures (and sometimes pressures) during the experiment itself or under disequilibrium conditions during quenching to ambient conditions (e.g., Ginther, 1971; Kimura et al., 1974; Campbell et al., 1989; Ertel et al., 1999; Cottrell and Walker, 2006; Mann et al., 2012).

If the PGE nuggets form at high temperature, then they are stable, discrete, equilibrium phases in the system, which should be reflected in a uniform spatial distribution (Borisov and Palme, 1997; Ertel et al., 1999, 2006; Yokoyama et al., 2009; Médard et al., 2015; Malavergne et al., 2016) and in their composition (Yokoyama et al., 2009). As the temperature decreases during quench, the solubility decreases in the sample as well, prompting crystallization (Brenan et al., 2016). Given enough time, i.e., a slow cooling rate, PGE should form nuggets during the quench phase. Evidence favors nuggets as stable high-temperature phases (e.g., O'Neill et al.,

1995; Médard et al., 2015; Malavergne et al., 2016), but no report confidently claims experiments to be completely devoid of quench nuggets.

There have been several attempts to address the nugget-formation-timing issue through different experimental protocols, e.g., Cottrell and Walker (2006) investigated Pt solubility and observed an increase in nugget diameter and change in spatial distribution and composition with decreasing cooling rates. This led them to conclude that the nuggets are a quench phenomenon. Médard et al. (2015) were able to separate out some nuggets by mounting a piston cylinder apparatus in a centrifuge and settling the nuggets on one side of their run products. If the nuggets had a quench origin, there would not have been time to transport them across the sample. Malavergne et al. (2016) revealed nuggets as inclusions within crystals, dendritic textures around nuggets and textural differences within the nuggets. Both Médard et al. (2015) and Malavergne et al. (2016) concluded nuggets are stable phases.

With the development of *in situ* geochemical analytical methods such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), the challenge of determining the nugget origin has only grown (Brenan et al., 2016). By using LA-ICP-MS, we are able to obtain a time-resolved signal of our sample, down to ppb levels of detection (Koch and Günther, 2016). Nuggets represent areas of high PGE concentration, and they manifest as peaks in the signal spectrum (Fig. 3.1.). LA-ICP-MS analysis highlights the nugget challenge: if nuggets formed at high temperature and are stable phases, they should be excluded from the analysis (e.g., Ertel et al., 2001, 2006; Laurenz et al., 2013), whilst if they formed during quench, they represent part of the true composition of the synthesized melt, and they should be included in the analysis (e.g., Cottrell and Walker, 2006).

The effect of including or excluding the nuggets in the final analysis can significantly influence the measured concentration of PGE in the melt. This would adversely affect the interpretation of our analysis if the nuggets were a stable phenomenon at high temperature and

should be excluded, i.e., one should use the troughs between the peaks (nuggets). This is not the case however, if the nuggets are a quench phenomenon, when the sample should be treated as a whole and all the area of the analysis should be considered for interpretation.



**Figure 3.1**. A simplified schematic representation of a hypothetical LA-ICP-MS signal. The x-axis represents the distance covered by a laser ablation line and the y-axis represents the counts per second (CPS) recorded. The thin grey line are actual counts, while the thick black line are averaged counts (averaged every 4 micrometers).

The abundance of evidence for nuggets as discrete phases at high temperature has led researchers (Borisov and Palme, 1997; Fortenfant et al., 2006) to hypothesize about their origin as a consequence of  $fO_2$  changes in the experiment, and Bennett et al. (2014) developed a model where HSE (highly siderophile elements: PGE + Au, Re) stable nugget formation is  $fO_2$  dependent. Experiments involving PGE and silicate melts are generally subject to an oxidation change. Initially, the glasses used in the experiments are synthesized in air, and the charges are are in most cases loaded in air and thus have high  $fO_2$ . Subsequently, at high-temperature and high-pressure conditions, they are subjected to a more reducing atmosphere in order to reflect

natural conditions. One way to achieve  $fO_2$  reduction at high-pressure and high-temperature (HPHT) is to load charges in graphite containers which also serve to avoid modification of the charge by the noble metal crucible often used in HPHT experiments (Bennett et al., 2014; Brenan et al., 2016). The initially high  $fO_2$  results in higher levels of PGE solubility; as the  $fO_2$  drops, the solubility decreases and the nuggets exsolve and stabilize as the  $fO_2$  stabilizes in the experiment (Bennett et al., 2014; Brenan et al., 2016).

Our aim was to test the whether the formation of PGE nuggets at high-temperature conditions is dependent on the oxygen fugacity change during the experiment or a change in HSE solubility during quenching by performing synchrotron radiation (SR) computed microtomography ( $\mu$ CT) experiments and numerical modeling. We prepared starting materials under oxidizing conditions and took them in a customized induction furnace where they were heated under reducing conditions. The samples were then imaged by X-ray SR  $\mu$ CT, prior to and after heating, to study nugget formation at different temperatures and experimental durations.

# 3.4. Materials and methods

The high temperature nugget formation hypothesis (Bennett et al., 2014) proposes that previously oxidized material takes time to reduce in the experiment and during this time the solubility of Pt drops and nuggets grow, as the  $fO_2$  stabilizes the nuggets stop growing and become stable in the melt (Fig. 3.2.). If the nuggets grow during quench the nuggets form because of the drop in solubility due to rapid cooling. Thus, we doped basalt glass with Pt by diffusion from a Pt capsule and heated this material in a custom-developed induction furnace available at the third generation Elettra synchrotron facility in Basovizza (Trieste, Italy). In particular, SR  $\mu$ CT experiments were performed in propagation-based, phase-contrast mode (Cloetens et al., 1997) at the SYRMEP beamline of Elettra (Tromba et al, 2010). The aim of these experiments was to use the fugacity gradient discovered in furnace testing (more on this in section 3.4.3) and the well characterized thermal history the furnace goes through during quench. Both were used to simulate the change in fugacity in the experiment as well as rapid cooling (quench) that is performed at the end of high temperature partitioning, solubility and diffusion experiments. Our oxidized sample is heated and reduced at the top of the sample and then rapidly cooled in the induction furnace. If the nuggets grow during oxygen fugacity reduction at high temperature they should preferentially form at the top of the sample near the meniscus – the contact between sample and the atmosphere. If they are formed during quench, they should be either homogeneously distributed thought the sample (if there is no appreciable gradient while cooling) or close to the center and bottom of the sample if there is a cooling gradient. The furnace can cool at the rate of 14 °C/s on average between 1400 °C and 600 °C. However, in our experiments we did not measure if there is a cooling gradient.


**Figure 3.2.** A schematic representation of Bennett et al.'s (2014) model of HSE-saturation dependence on oxygen fugacity (the figure is a simplification of Figure 2 in Bennett et al., 2014). The temperature is constant. Initial time  $(t_1)$ : the initially oxidized sample starts to become reduced. There is no HSE nugget formation, as HSE-oversaturation of the system is not yet achieved. Intermediate time  $(t_2)$ : oxygen fugacity is still dropping and the melt becomes oversaturated in HSE. Nuggets begin to form and grow. Final time  $(t_3)$ : oxygen fugacity stabilizes and the nuggets reach equilibrium with the melt.

# **3.4.1. Starting material preparation**

The starting material was prepared at McGill University (Montréal, Canada), using Etna basalt (Alletti et al., 2007). Preliminary experiments were first performed to determine the time required to saturate the basalt with Pt at McGill and to determine the viability of the experimental set-up at Elettra.

The basalt was loaded into a large Pt crucible (diameter 1 cm) and heated in air in a box furnace at 1300 °C for 72 hours. The products were manually removed from the Pt crucible, re-crushed and heated again for another 72 hours. The process was repeated until the total heating time was 288 hours (12 days), because at shorter melting durations, nuggets were discovered within the samples (by using SEM-EDS; scanning electron microscopy electron dispersive spectroscopy). Great care was taken to minimally damage the Pt crucible while extracting material from it and material (glass) clinging to the walls of the crucible that resisted removal was discarded. The goal was to avoid contamination by the crucible material (Pt) which would be difficult to distinguish from the nuggets. After 288 hours, a sample was analyzed by SEM and LA-ICP-MS, to check for the presence of nuggets and dissolved Pt in the melt. An additional final heating was performed to further mitigate contamination by the Pt crucible; this Pt-saturated glass was placed in an alumina crucible (matching those used by the Elettra induction furnace; Kudrna Prašek et al., 2018) and heated again for 72 hours at 1350 °C. This final heating step was performed to allow Pt metal contaminants to settle to the bottom of the crucible and any air bubbles to escape, to minimize phase interference during high temperature X-ray scanning at SYRMEP. A single prepared sample was scanned using a conventional µCT instrument, Skyscan 1172 (Bruker, USA), available at MIAM (McGill University). The scanning conditions were the following: Voltage = 70 kV, current = 141  $\mu$ A, Al+Cu filtering (0.58 mm total thickness), detector binning  $2x^2$ , source-to-sample distance = 55.87 mm, source to detector distance = 228.478 mm, detector pixel size =  $12.06 \mu$ m, effective pixel size = 5.9  $\mu$ m, exposure time per projection = 1180 ms, rotation step = 0.25 °, total scan angle =  $180^{\circ}$  + fan angle, frame averaging = 3). The goal was to check for the presence of bubbles, which were not found after the 72 h heating. The loaded alumina crucibles were then taken to the SYRMEP beamline at Elettra.

## 3.4.2. Starting material characterization

Some of the starting material was separated prior to the final 72-hour heating at McGill University for SEM-EDS analysis. The aim was to determine the glass composition, to check for element loss (e.g., Fe) and for nugget presence. We wanted to ascertain that 288 hours are sufficient to generate a Pt-saturated but nugget-free melt. The samples were analyzed at McGill University (Montréal, Canada) with a Hitachi SU5000 Schottky Field Emission scanning electron microscope equipped with an Oxford X-MAX80 EDS detector. A 15 kV accelerating potential and 0.134 mA beam current were used.

Nuggets were not detected in the 288 h-starting material, investigated by SEM. This is unsurprising because if there are few nuggets in the entire sample, the chance to detect them in a random plane is low. However, in the preliminary experimental run products (those performed before we settled on a 288-h heating duration), two nuggets were detected (Fig. 3.3). Their composition, ~ 90 % Pt and ~ 8 % Fe, is included in Figure 3.3. Both nuggets are euhedral in shape and 5 and 7  $\mu$ m across. This result was unexpected, as nuggets are not thought to form under oxidizing conditions (Campbell et al., 1989). The glass composition, obtained by SEM-EDS, differs from the composition of Alletti et al. (2007) obtained by electron microprobe. FeO, MgO, CaO and K<sub>2</sub>O have decreased (FeO is 10.24 wt. % compared to 10.57±0.09 wt. %, MgO is 4.38 wt. % compared to 6.32±0.09 wt. %, CaO is 9.99 wt. % compared to 10.83±0.10 wt. %, K<sub>2</sub>O is 1.50 wt. % compared to 1.78±0.03 wt. %), while TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Na<sub>2</sub>O have increased from the reported values (TiO<sub>2</sub> is 1.72 wt. % compared to 1.63±0.05 wt. %, Al<sub>2</sub>O<sub>3</sub> is 19.88 wt. % compared to 16.93±0.09 wt. %, Na<sub>2</sub>O is 3.98 wt. % compared to 3.62±0.05 wt. %). It is to be noted that the SEM-EDS analysis is semiquantitative since no standards were used to calibrate the analysis; it is only used to confirm the nuggets are indeed Pt nuggets.



**Figure 3.3.** SEM-BSE images of the nuggets and SEM-EDS semi-quantitative analysis results. The values are expressed as wt. % and are normalized to 100. Both nuggets are euhedral. A) SEM-BSE image containing two nuggets along with the glass composition. B) and C) Enlarged SEM-BSE images of the individual nuggets in panel A, with their individual compositions.

Additional starting material (also separated prior to the final 72-hour heating) was analyzed by LA-ICP-MS at LabMaTer (Université du Québec à Chicoutimi, Canada) using the Resolution M-50 (193 nm) laser ablation system combined with ICP-MS 7900x Agilent ICP-MS. The goal was to accurately measure the value of Pt dissolved in the glass. Elements <sup>24</sup>Mg, <sup>27</sup>Al, <sup>29</sup>Si, <sup>34</sup>S, <sup>35</sup>Cl, <sup>49</sup>Ti, <sup>51</sup>V, <sup>53</sup>Cr, <sup>55</sup>Mn, <sup>57</sup>Fe, <sup>59</sup>Co, <sup>61</sup>Ni, <sup>65</sup>Cu, <sup>66</sup>Zn, <sup>75</sup>As, <sup>82</sup>Se, <sup>101</sup>Ru, <sup>102</sup>Ru, <sup>103</sup>Rh, <sup>108</sup>Pd, <sup>185</sup>Re, <sup>187</sup>Re, <sup>189</sup>Os, <sup>191</sup>Ir, <sup>193</sup>Ir, <sup>195</sup>Pt and <sup>197</sup>Au were monitored in the analysis package. Spot size was 10 x 150  $\mu$ m, with a frequency of 15 Hz and fluence from 5 J/cm. Gas blank acquisition lasted for 30 seconds and the laser ablation lasted for 30 seconds. The sample cell was flushed with He and N<sub>2</sub>. Measurements of element concentrations were calibrated with the Fe-sulfide Laflamme-Po727 (Pagé and Barnes, 2016) using <sup>57</sup>Fe to calculate the ablation yield and cross-checked using doped glasses GSE (Jochum and Nohl, 2008) and NIST 610 (Pearce et al., 1997; Jochum et al., 2011). Calibration was checked with the GSE yielding results within the error of Po727.

The starting material heated at 1300 °C for 288 h had a Pt concentration of 8.22 ppm. Additionally, 13.1 ppm of Au and 0.29 ppm of Pd were found. Similar to the Pt, the origin of the Au and Pd is likely the Pt capsule, however at this time no Au or Pd nuggets were found by SEM and we have not analyzed the Pt capsule for other PGE. The control GSE glass yields a Pt content of 22.5 to 27 ppm with the single anomalous analysis of 14.3 ppm when calibrated with Fe-sulfide Laflamme-Po727. The NIST 610 glass yields 3.03 ppm when calibrated with Fe-sulfide Laflamme-Po727. The NIST glass preferred Pt value is 3.12 ppm and the GSE preferred value is 30 ppm, however, when calibrating with Fe-sulfide Laflamme-Po727 in experience of these authors values obtained are around 25 ppm.

### **3.4.3.** Synchrotron radiation µCT experiments

# Induction furnace setup at Elettra

The high temperature induction furnace developed at Elettra (Kudrna Prašek et al., 2018) functions by inducing circular electric currents in a susceptor, an electrically conductive and resistive material – in this case graphite, by creating a magnetic field using an induction coil. The susceptor heats up due to high resistivity and transfers the heat to the crucible and the sample. The furnace consists of the induction coil in the center of which the susceptor and crucible is placed. The coils are spaced at the center such that a 6 mm gap is available for the X-rays to pass through, but the furnace still creates in this region a uniform magnetic field for heating. The graphite susceptor stands on a zirconia rod and is shaped in such a way that a crucible fits inside. The gas used to protect the graphite is N<sub>2</sub>. Different combinations of graphite susceptor sizes and parts can be used (Fig. 3.4). It was hypothesized this could be used as a preliminary  $fO_2$  control, as the planned CO-CO<sub>2</sub> gas system mixing for the furnace was still in development. Configurations that include susceptor pieces 1 or 2, combined with the alumina crucible (piece 4), i.e., 1+4 or 2+4 in Figure 3.4, produce a gradient of the  $fO_2$  in the sample. The experiments presented here (Table 3.1) were completed using the configuration 1+4. Different configurations of the graphite susceptor were tried during the commissioning and tested for change in  $fO_2$  and temperature calibration and gradient.



**Figure 3.4.** Different susceptor pieces compatible with the Elettra induction furnace (Kudrna Prašek et al., 2018). In grey are graphite pieces and in white is an alumina crucible. Pieces 1-3 have the same upper diameter aperture but different lengths, which allows for some  $fO_2$  control.

**Table 3.1.** Run table of the 24 *in situ* scans on 12 samples, each sample was scanned before and after heating. Samples were heated to 1400, 1350, 1300 and 1250 °C, for 4 or 1 hour. h = hour.

Sample name	Heating time (h)	Temperature °C
MKP14	4	
MKP15	4	1400
MKP16	1	
MKP17	4	
MKP18	4	1350
MKP19	1	
MKP20	4	
MKP21	4	1300
MKP22	1	
MKP23	4	
MKP24	4	1250
MKP25	1	

The graphite susceptor used in the furnace will influence the oxygen fugacity of the sample in the furnace. Initial testing revealed that in the standard mode of operation (graphite pieces 1+5 in Fig. 3.4) a sample containing nickel oxide (NiO) powder turns entirely to Ni in less than 30 minutes at 1300 °C, indicating that the sample oxygen fugacity with the furnace in this configuration is below  $\log fO_2 = -6.6988$  (O'Neill and Pownceby, 1993). Using the furnace with the "top off" (pieces 1+4 in Fig. 3.4) allows more N<sub>2</sub> flow to reach the sample and then only the top 0.11 mm of the NiO turns to Ni, even after 4 h at 1400 °C (Fig. 3.5). Consequently, we used only graphite piece 1 in the furnace to impose a  $fO_2$  gradient on our samples and used it to test the stability of Pt nuggets at high temperatures



**Figure 3.5.** Oxygen fugacity gradient imposed within the samples. A) Schematic cross section of the alumina crucible (in white). In light green the range of positions of the bottom of the meniscus created by the basalt melt in all samples is shown. The relative position of the oxygen fugacity gradient in the samples is shown in dark green. The vertical extent of the fugacity gradient is 0.11 mm. B) Transversal section obtained by X-ray  $\mu$ CT of the capsule and the meniscus. C) Oxygen fugacity testing experimental run product using the furnace configuration used through this study (1+4 in Fig. 3.4).

## Synchrotron radiation X-ray µCT imaging

The nugget 3D imaging experiments were performed at the SYRMEP beamline of Elettra, working in filtered white beam (pink beam) mode with the sample stage located ca. at 240 mm from the source and with a maximum vertical beam size at the sample location of 160 mm (h) x mm (v). Horizontal and vertical slits were used to tailor the beam size according to the imaged region of interest. Images were acquired using an air-cooled, 16-bit, 2048 x 2048 pixel, macroscope camera based on a sCMOS detector (Hamamtsu C11440-22C) lens-coupled with a 17  $\mu$ m-thick GGG scintillator screen.

A multi-scale experimental approach was used. X-ray scans were initially performed at 2.4  $\mu$ m pixel edge length and subsequently at a 0.9  $\mu$ m pixel edge length in the area of interest. Lower resolution 2.4  $\mu$ m scans were intended to find the area of interest and confirm the nugget position. These scans were performed with 1500 projections and the exposure time of 0.2 and 0.3 s. In order to maximize data quality, additional scans were performed setting the pixel size at 0.9  $\mu$ m acquiring 1800 projections per scan and with an exposure time ranging from 0.3 to 0.4 s. All results presented in the figures are from scans performed at the higher spatial resolution.

#### Problems with real-time scanning

The final 72 h melting in the alumina crucible was mostly intended to release all the bubbles from the melt in order to prevent bubble movement during the high-temperature *in situ* X-ray  $\mu$ CT scan, as seen in preliminary experiment results. This movement would cause strong artefacts in the tomographic reconstructed images. Unfortunately, on most experimental charges used in the final experiments at Elettra, bubbles adhered to the crucible wall. When the samples were heated at Elettra using the induction furnace, the bubbles were released from the crucible walls because of the fast rotational sample movement before the tomography scan to

arrive at the scanning position. Thus, some small bubbles still affected the quality of the *in situ* and real time high-temperature imaging. Consequently, the high-temperature *in situ* and real time scanning results for the selected experiments were not usable and only *in situ* scans at room temperature were utilized to study the nugget distribution and the nugget relative size before and after heating.

### 3.4.4. Reconstruction of microtomographic data

The acquired sample radiographs (projections), after flat-field correction, were reconstructed using the STP software suite custom-developed at Elettra (Brun et al., 2015). The 32-bit .tif reconstructed images were converted to 8-bit grayscale .tif format since the latter's dynamic range was sufficient for the processing and analysis protocol required for this particular case. The Pt nuggets are dense and highly absorb X-rays, providing a large contrast with the surrounding glass, which makes them easily distinguishable. Due to the high X-ray absorption of Pt and the use of the propagation-based, phase-contrast, imaging modality, even nuggets smaller than the detector pixel size were captured (Fig. 3.6; Baruchel et al., 2000). A single-distance phase retrieval algorithm (Paganin et al., 2002) was applied to the acquired projection images prior to the tomographic reconstruction using the STP software and a  $\delta/\beta$  ratio ( $\delta$  and  $\beta$  being, respectively, the real part and imaginary parts of the refraction index of the material under investigation) of 50. The reconstructed stacks of images were analyzed using Fiji (Schindelin et al., 2012) and Pore3D (Brun et al., 2010).

### 3.4.5. 3D data processing and analysis

The bleeding out effect, where surrounding voxels are affected by a single voxel of very high intensity (Fig. 3.6B; Baruchel et al., 2000), was present in the reconstructed images. When applying thresholding, i.e., selecting the grayscale range of the nugget phase in the

reconstructed volume, the nugget size had to be overestimated in order to capture all the nuggets. This was necessary because when a conservative threshold was applied to larger nuggets (e.g., 8 µm diameter, Fig. 3.6A), the nuggets smaller than 1 voxel, that are detectable only through their bleed out halo (Fig. 3.6B; Baruchel et al., 2000), were not selected. The thresholding range was thus increased until 1 voxel in the center of the halo was selected. Consequently, the individual nugget volume is overestimated. To attempt to quantify the degree of overestimation, a volume comparison of larger nuggets was performed: a large nugget (e.g., Fig 3.6A) was thresholded using conservative threshold values and using the increased threshold values. The difference in volume on average corresponds to a spherical shell 3 voxels thick, i.e., the average overestimation is 3 voxels in x, y and z directions. However, this problem was not present in all samples, and we have prioritized determination of nugget numbers over nugget volumes. Consequently, we chose to report relative - overestimated - nugget volumes instead of absolute ones.



**Figure 3.6.** Comparison of nuggets in 8-bit reconstructed axial slices from sample MKP16, after heating. A) a large nugget with a 8  $\mu$ m diameter, B) a small nugget with a  $\leq 0.9 \mu$ m dimeter, seen only as a halo. Even if the nugget in panel B has a true size smaller than the achievable spatial resolution, it is detectable due to the bleeding effect (Baruchel et al., 2000).

### 3.5. Results

# 3.5.1. Nugget numbers

The section 3.4.1 discusses how the starting material was prepared and loaded into the alumina crucibles. In short, the glass was saturated with Pt at 1300 °C, loaded into the alumina crucibles and heated again for 72h at 1350 °C. As per previous testing experiments, the nuggets are expected to form in the starting material, since the glass was saturated at 1300 °C we expect nugget crystallization in the entire sample to start below 1300 °C.

Before heating to 1400 °C samples MKP14, MKP15 and MKP16 had 19, 7 and 44 nuggets, respectively (Fig. 3.7). After heating for 4 h at 1400 °C samples MKP14 and MKP15 have 18 and 25 nuggets, respectively. After heating for 1 h at 1400 °C sample MKP16 has 25 nuggets.

Before heating to 1350 °C samples MKP17, MKP18 and MKP19 had 28, 11 and 43 nuggets, respectively (Fig. 3.7). After heating for 4 h at 1350 °C samples MKP17 and MKP18 have 24 and 31, respectively. After heating for 1 h at 1350 °C sample MKP19 has 41 nuggets.

Before heating to 1300 °C samples MKP20, MKP21 and MKP22 had 37, 5 and 13 nuggets, respectively (Fig. 5.7). After heating for 4 h at 1300 °C samples MKP20 and MKP21 have 77 and 5 nuggets, respectively. After heating for 1 h at 1300 °C sample MKP22 has 7 nuggets.

Before heating to 1250 °C samples MKP23, MKP24 and MKP25 had 36, 19 and 38 nuggets, respectively (Fig. 3.7). After heating for 4 h at 1250 °C samples MKP23 and MKP24 11 and 16 nuggets, respectively. After heating for 1 h at 1250 °C sample MKP25 has 30 nuggets.

At temperatures higher than the saturation temperature of these experiments (1300 °C), i.e., 1400 and 1350 °C, the nugget number in sample MKP 16 after heating is smaller, but close to the nugget number after heating in samples MKP 14, 17 and 19. However, the nugget number

after heating in sample MKP 16 is higher than in samples MKP 15 and 18, after heating, as shown in Figure 3.7.

At the saturation temperature (1300 °C), after 1 h of heating (AH), the nugget number has slightly decreased when compared to the nugget number before heating (BH), 7 vs. 13, respectively. After 4 h of heating, the nugget number is higher in sample MKP 20 (77 vs. 37, respectively), and the same in sample MKP 21 (5).

Heating to 1250 °C for 1 and 4 h produces a smaller number of nuggets after heating. To summarize, after 1 hour of heating, there are always less nuggets than before heating, for all four experiments. After 4 hours of heating, samples MKP15, MKP18 and MKP20, at 1400 °C, 1350 °C and 1300 °C, respectively, exhibit more nuggets after heating.



**Figure 3.7.** Number of nuggets before and after heating for 1 h and 4 h duration experiments. In all samples, there are nuggets before heating. After 1 hour of heating, there are fewer nuggets than before heating for all experiments. After 4 hours of heating, at 1400 °C, 1350 °C and 1300 °C, in one out of two experiments at each temperature, there are more nuggets than before heating.

### **3.5.2.** Nugget volume

The nugget volumes per sample are given in Table 3.2. Both the arithmetic mean (average in the table) and median volumes are given, since often in these samples one large grain or large number of small grains will skew the average, so both will be mentioned if appropriate. After heating at 1400 °C for 4 h, in samples MKP14 and MKP15, the total nugget volume is smaller than before heating. However, after heating at 1400 °C for 1 h, in sample MKP16, it is larger (n.b., this is if the median total volume values are compared, if the average total volumes are compared the nuggets are smaller after heating). After heating at 1350 °C for 1 h (MKP19) they are larger (at 1350 °C both median and average total volume are larger after heating). After heating at 1300 °C for 4 h, in both samples MKP20 and MKP21 the average nugget volumes are larger. The same holds after heating at 1300 °C for 1 h in sample MKP23 and MKP24, but the median nugget volume after heating is larger in sample MKP23 and smaller in sample MKP24. After heating at 1250 °C for 1 h in sample MKP25 the nuggets have the same median volume, but the average volume is larger before heating.

To summarize, across all temperatures and all heating durations, the average nugget volume is larger after heating in only 4 samples out of 12: MKP18 (1350 °C, 4h), MKP19 (1350 °C, 1h), MKP20 (1300 °C, 4h) and MKP21 (1300 °C, 4h). The median nugget volume is larger after heating in 5 samples: MKP16 (1400 °C, 1h), MKP19 (1350 °C, 1h), MKP21 (1300 °C, 4h), MKP22 (1300 °C, 1h) and MKP23 (1250 °C, 4h).

**Table 3.2.** Nugget sizes before and after heating. Data is shown for all nuggets in a given sample, not for individual ones. Samples MKP16, MKP19, MKP22 and MKP25 were heated for 1 h, while others were heated for 4 h. The "total" row presents the total maximum, average and median nugget volumes. "a length" row presumes the nugget to be a cube (V =  $a^3$ ) and "r length" presumes the nugget to be a sphere (V =  $\frac{4}{3}\pi r^3$ ). Both are presented because in much of the previous literature it is either not stated what the nuggets size is or it is unclear. Max = maximum, sd = standard deviation.

	ВН				AH						
Temperature (°C)	Sample name	MAX	Average	Median	Sd (µm <sup>3</sup> )	MAX	Average	Median	Sd (µm <sup>3</sup> )		
		volume	volume	volume		volume	volume	volume			
		(µm <sup>3</sup> )	(µm <sup>3</sup> )	$(\mu m^3)$		$(\mu m^3)$	(µm <sup>3</sup> )	$(\mu m^3)$			
1400 °C	MKP 14	1850	338	163	480	392	113	92	120		
	MKP 15	3233	1034	1173	1166	1217	236	2	381		
	MKP 16	13601	993	227	2772	2273	531	277	617		
	Total	13601	789	227	1176	2273	294	92	249		
	a length µm	23.87	9.24	6.10	10.56	13.15	6.65	4.52	6.29		
	r length µm	14.81	5.73	3.79	6.55	8.16	4.12	2.80	3.90		
1350 °C	MKP 17	3608	668	215	921	7706	570	11	1610		
	MKP 18	2633	1205	1370	875	11684	1585	320	2780		
	MKP 19	3734	536	282	739	5659	799	299	1296		
	Total	3734	803	282	95	11684	985	299	782		
	a length µm	15.51	9.29	6.56	4.56	22.69	9.95	6.69	9.21		
	r length µm	9.62	5.77	4.07	2.83	14.08	6.17	4.15	5.72		
1300 °C	MKP 20	7355	762	419	1258	24279	795	2	2919		
	MKP 21	521	193	129	204	1993	803	360	913		
	MKP 22	5364	1496	507	1884	3900	1374	884	1484		
	Total	7355	817	351	1115	24279	991	415	1772		
	a length µm	19.45	9.35	7.06	10.37	28.96	9.97	7.46	12.10		
	r length µm	12.06	5.80	4.38	6.43	17.96	6.18	4.63	7.51		
		-									
1250 °C	MKP 23	15480	1096	17	2801	3291	702	299	963		
	MKP 24	50742	4426	674	11652	6765	748	325	1639		
	MKP 25	24846	1591	190	4195	7554	678	190	1528		
	Total	50742	2371	294	6216	7554	709	272	1377		
	a length µm	37.02	13.33	6.65	18.39	19.62	8.92	6.48	11.12		
	r length µm	22.97	8.27	4.12	11.41	12.17	5.53	4.02	6.90		

## **3.5.3.** Nugget location

Determining the nugget location in *in situ* experiments is crucial due to the imposed oxygen fugacity gradient when heating with the Elettra induction furnace. The meniscus formed by the melt at high temperatures is used as the orientation point since it is not located at the same height in all experimental charges, so the bottom of the crucible cannot be used as an orientation point. The fugacity gradient appears at the surface of the sample so the meniscus location is much more vital to nugget formation than the bottom of the crucible. Nuggets appear within 0.92 mm of the meniscus, often much closer (Fig. 3.8). To illustrate better the heterogeneous nugget location, it is worth noting they only appear 2.47 mm from the bottom of the crucible, before and after heating. The distance from the bottom cannot be used as the measurement for the precise nugget location as mentioned previously, but can be used to illustrate the heterogeneous nugget distribution.

Before heating for 1 h at 1400 °C sample MKP16 has a unimodal distribution with a peak 0.23 mm below the meniscus, slightly skewed towards the meniscus (Fig. 3.8A). After heating sample MKP16 there are more nuggets away from the meniscus (heavily skewed to the right). Before heating for 1 h at 1350 °C sample MKP19 has a unimodal distribution of nuggets with no pronounced peaks, but all nuggets are close to the meniscus, within 0.23 mm. After heating, there are more nuggets closer to the meniscus, within 0.14 mm (Fig. 3.8B). Before heating for 1 h at 1300 °C sample MKP22 nuggets are unimodally distributed from 0.11 to 0.36 mm away from the meniscus, with a weak peak at 0.23 mm away. After heating the are nuggets closer to the meniscus, 0.28 mm (Fig. 3.8C). Before heating for 1 h at 1250 °C sample MKP25 has a unimodal nugget distribution, skewed closer to the meniscus, without a very pronounced peak. The distribution does not change after heating but there are more nuggets close to the meniscus, seen in a peak  $\leq 0.11$  mm from the meniscus (Fig. 3.8D).



**Figure 3.8.** Nugget location before and after heating for 1 h. The distances shown in panels A, B, C and D are distances from the meniscus to estimate the effect of the oxygen fugacity gradient imposed on the samples. The fugacity change limit is depicted by a dashed line. After heating, samples MKP19 and MKP25 have distributions skewed towards the meniscus, sample MKP22 has nuggets slightly closer to the meniscus, but sample MKP16 shows a distribution skewed away from the meniscus.

The data in Figure 3.9 shows the effect of the heating duration of 4 h. After heating at 1400 °C, the nugget distribution in sample MKP14 changed from unimodal without pronounced peaks to bimodal with strong peaks  $\leq 0.11$  mm and  $\geq 0.41$  mm away from the meniscus (Fig. 3.9A), while in sample MKP15 it changed from unimodal without strong peaks to unimodal skewed closer to the meniscus with a peak at 0.16 mm away from the meniscus (Fig. 3.9B).

After heating at 1350 °C, the nugget distribution in sample MKP17 changed from unimodal away from the meniscus to almost a single pronounced peak  $\leq 0.11$  mm from the meniscus (Fig. 3.9C), while in sample MKP18 it changed from unimodal between 0.11 and 0.26 mm, with a pronounced peak at 0.18 mm, to weakly bimodal with peaks at 0.188 mm and 0.38 mm away from the meniscus (Fig. 3.9D).

After heating at 1300 °C, the nugget distribution in sample MKP20 changed from slightly bimodal, with two weak peaks at  $\leq 0.11$  mm and 0.28 mm, to strongly bimodal with pronounced peaks at 0.23 mm and 0.38 mm away from the meniscus (Fig. 3.9E), while sample MKP21 has 5 nuggets between 0.11 and 0.42 mm from the meniscus (Fig. 3.9F).

After heating at 1250 °C, the nugget distribution in sample MKP23 changed from unimodal skewed closer to the meniscus to non-skewed unimodal centered at 0.18 mm, but with fewer nuggets (Fig. 3.9G), while in sample MKP24 it changed from a plateau distribution from  $\leq 0.11$  to 0.33 mm to a single pronounced peak close to the meniscus at  $\leq 0.11$  mm (Fig. 3.9H).



**Figure 3.9.** Nugget location before and after heating relative to the meniscus. The fugacity change limit is depicted by a dashed line. Nuggets after heating show a distribution skewed towards the meniscus (panels A, B, C, D, F, G and H), except for the sample MKP20 in panel E.

### **3.6.** Discussion

Nugget formation in experimental charges is hypothesized to be due to a change in oxygen fugacity during the experiment or during quenching (Bennet et al., 2014). The SEM results in this study show the nuggets in the starting material to be euhedral, which indicates high temperature formation. The LA-ICP-MS analysis shows high Pt content (8 ppm) in the glass before loading in the alumina crucibles; therefore, there is Pt available for nugget formation under reducing or quenching conditions.

Surprisingly, before heating with the induction furnace at Elettra in a lower  $fO_2$ environment (< NNO), melts are not nugget-free as could be expected due to their synthesis under highly oxidizing conditions in air (Campbell et al., 1989). Additionally, the starting material was prepared at 1300 °C, then loaded in alumina capsules and heated again in air at 1350 °C. It was expected that most nuggets would be eliminated by this process, and any potential contamination from the capsule wall, that we were perhaps unable to avoid, would sink to the bottom of the crucible. The location of these nuggets is surprising as well. The starting material saturated with PGE and containing nuggets, as confirmed by SEM, was loaded as chips into the alumina crucible and melted for 72 h to get rid of the bubbles and allow the nuggets to sink to the bottom. However, all nuggets are located close to the meniscus even after 72 h of heating. This is unexpected as all nuggets larger than 4.4  $\mu$ m in radius should have sunk to the bottom of the crucible. Possibly the nuggets were transported to the top of the meniscus by the bubbles, but we do not find any bubbles with the nuggets attached, and still many larger nuggets would have time to sink so one would expect some kind of distribution of nuggets before heating in the induction furnace from larger to smallest as one gets close to the meniscus which is not what we find, more on the position and size distribution can be found in the section 3.6.3. This, apparently dynamic process, highlights the need for real time studies.

### **3.6.1.** Nugget numbers at different temperatures

Heating for 1 h at 1400 °C produces a smaller number of nuggets as expected since the melt is undersaturated at this temperature (sample MKP16, Fig. 3.7A), but at 4 h the nugget number is barely smaller after heating sample MKP14, and it has more than doubled in sample MKP15 (Fig. 3.7B). The pattern is unchanged at 1350 °C (samples MKP17-19) and 1300 °C (samples MKP20-22, Fig. 3.7). After the 1250 °C heating, all samples (MKP23-25) show a decrease in nugget number (Fig. 3.7).

The loss of nuggets during the lowest temperature heating is unexpected as undercooling should decrease solubility and yield more nuggets. It appears that in the higher temperature experiments, the imposed fugacity gradient promotes nugget formation, but only in one experiment at 1400 °C, 1350 °C and 1300 °C each, during 4 h. Interestingly, there is less variation in nugget number and the overall number is always smaller before and after heating in the shorter experiments (1 h) suggesting the fugacity gradient increases over time (Fig. 3.7). This suggests that it takes more time for the fugacity gradient to take effect when imposed on the silicate melt than NiO, as it changes to Ni on the surface in less than 30 minutes.

# 3.6.2. Nugget size distribution change

All nuggets larger than 3375 voxels (or  $3037.5 \ \mu m^3$ ) are not considered. This corresponds to 15 voxels across (13.5  $\mu$ m). The rationale is that nuggets larger than 15  $\mu$ m have not been reported in the literature and could be leftover contamination from the Pt crucible. Out of the total 610 nuggets, 37 were removed.

Nugget volumes are variable, but not irregular. In Figures 3.10 and 3.11 the nugget volume is recalculated to cube border length (a). This was done to conform to previously published literature and make comparison readily available to the reader. The short, 1 h experiments MKP16 (1400 °C) and MKP19 (1350 °C) display unimodal distributions and show

no large changes in volume before and after heating (Fig. 3.10A, B). Sample MKP22 (1300 °C) retained a bimodal volume distribution with unchanged peak locations, both before and after heating (Fig. 3.10C). In the 1250 °C experiment (sample MKP25) the number of nuggets of sizes  $6 - 8 \mu m$  is greatly increased (Fig. 3.10D). It is possible this is due to the temperature being lower than the synthesis temperature of 1300 °C and thus Pt saturation is expected. As stated previously, only relative size will be considered due to possible nugget size overestimation, therefore small (1 or 2 nuggets and 1 or 2 microns depending on the overall number and size) changes in size and number will be ignored. It is however notable that the number of small (up to 4  $\mu m$ ) nuggets is lower after heating in all experiments except MKP19 (1350 °C) experiment (Fig. 3.10B).



**Figure 3.10.** Size (cube side - a – calculated from the nugget volume) distribution of nuggets before and after 1 h heating. BH = before heating, AH = after heating.

The 4h experiments display a different pattern. In all (Fig. 3.11A-F) but the lowest 1250 °C temperature experiments (Fig. 3.11G and H) the number of small (up to 4  $\mu$ m) nuggets has increased after heating. This potentially points to the formation of new nuggets due to the change in *f*O<sub>2</sub>. It could however also point to the dissolution of bigger nuggets in the higher temperature experiments, which is also indicated by the drop in average and median volume before and after heating (Table 3.2).



**Figure 3.11.** Size distribution of nuggets before and after 4 h heating. BH = before heating, AH = after heating.

### **3.6.3.** Nugget location relative to the position of the meniscus

In our experiments, the nuggets only appear 2.47 mm from the bottom of the crucible. If the nuggets are forming when the sample is undergoing quenching, we can assume an even distribution within the sample if no thermal gradient during cooling is present, or preferential distribution towards the center of the sample to account for the slower cooling closer to the center of the sample (Cottrell and Walker, 2006). When discussing our results, we emphasize that the number of nuggets present is still relatively low when compared to previously published literature (e.g., see Figures 1 and 2 from Malavergne et al., 2015 or Figures 2 and 3 from Cottrell and Walker, 2006). The nugget number is however difficult to compare to other studies, due in part to inherent difficulties when comparing 2D and 3D data, but also because numbers may simply not be provided (e.g., Cottrell and Walker, 2006; Malavergne et al., 2015). As our spatial resolution is ~ 2  $\mu$ m (2 voxels) we likely missed the nuggets far below our spatial resolution, and the lower range of detection is difficult to estimate due to the high X-ray absorption (as discussed previously). However, using nondestructive 3D imaging we have a better chance of capturing a sparse and unevenly distributed nugget population.

The 1 h experiments results are inconclusive. At 1400 °C and 1300 °C there are more nuggets close to the meniscus (or a similar number) before than after heating (Fig. 3.12). However, the 1350 °C and 1250 °C results clearly show that after heating nuggets appear closer to the meniscus. Since the nugget number and size are smaller after heating, the case cannot be made that nuggets appear due to the change in  $fO_2$  in the first hour. It is possible the  $fO_2$  of the sample did not have enough time to equilibrate with the graphite susceptor.

The higher temperature 4 h experiments are more conclusive. The number of small nuggets close to the meniscus after heating is larger than before heating at 1400 °C and 1300 °C (Fig. 3.11 and Fig. 3.13). This indicates that the longer heating time allows the reducing atmosphere to take effect and impose the gradient that in turn lowers the Pt solubility and

precipitates the nuggets. Sample MKP14 has small nuggets both close to the meniscus and far away (Fig 3.12A).

Using the Stokes sinking velocity equation and calculating the melt viscosity at 1300 °C ( $\eta = 11.22$  Pa/s, Giordano et al., 2008), given the known composition of the Etna basalt, we calculate that the maximum distance the largest nugget settles during the 4-hour experiment is 18.2 mm, and the average is 1.77 mm. Calculating the settling distance for 1300 °C is intentional as the nuggets already present in the melt shouldn't grow, unless they are in the low  $fO_2$  area, and should settle uniformly. However, we do not observe the settling in any sample. At 1300 °C the lowest nugget, i.e., furthest away from the meniscus, is 0.6 mm from the meniscus. We think that there is either convection in the crucible, which is unlikely as this would deposit the nuggets randomly around the capsule, or that the bubbles with nuggets attached moved to the top of the melt. The latter explanation is also not complete as no nuggets were observed attached to the bubbles and many nuggets observed before heating are found again close to their location after heating.



**Figure 3.12.** Nugget position vs. the nugget number and size in 1h heating experiments. The light gray points indicate nuggets before heating, and the black points indicate nuggets after heating. The dashed line indicates the likely beginning of the reducing  $fO_2$  gradient and the effect is more reducing above the line. BH = before heating, AH = after heating. The meniscus distance value zero indicates the bottom of the meniscus while the negative meniscus distance values indicate higher positions as the meniscus curves upward.



**Figure 3.13.** Nugget position vs. the nugget number and size in 4 h heating experiments at 1400 and 1350 °C. BH = before heating, AH = after heating. The meniscus distance value zero indicates the bottom of the meniscus while the negative meniscus distance values indicate higher positions as the meniscus curves upward.

The lower temperature (1300 and 1250 °C) 4 h experiments are inconclusive. At 1300 °C the overall nugget number increases (Fig. 3.7), on average the volume increases, however the number of nuggets close to the meniscus does not increase in sample MKP20, but does in MKP21 (Fig 3.14A and B). Sample MKP20 does show an increase in small sized nuggets, but further away from the meniscus (Fig. 3.14A). The samples were saturated with Pt at 1300 °C during preparation, so it is expected that their number grows at this temperature due to the influence of  $fO_2$  change, and it does, but in the case of MKP20 not as close to the meniscus as expected. The 1250 °C results are similar to those at 1300 °C, more so in sample MKP24 than MKP25, and show the nuggets after heating closer to the meniscus (Fig 3.14C and D) The slight undercooling (1250 °C) from the Pt-saturation temperature (1300 °C) was expected to produce more or larger nuggets, but this was not the case.

The proposed hypothesis by Bennett et al. (2014) of nugget formation by decrease in  $fO_2$  of the initially oxidized starting material requires the nuggets to form in the area of influence of the imposed fugacity gradient. We have determined the development of the fugacity gradient through NiO to Ni transition experiments and in the majority of our experiments, nuggets formed within the gradient. However, the inconclusive 1 h experiment results might indicate that the fugacity gradient requires more time to take effect. Nugget formation in the lower  $fO_2$  area is also more prominent at higher temperatures, which could be due to faster  $fO_2$  change with the melt. Using the measured oxygen diffusivities in basalt from

Lesher et al. (1996) we can calculate that the oxygen should have diffused to 0.14 mm after 1 hour at 1250 °C and 0.28 mm after 4 hours, and at 1400 °C for 1h to 0.26 mm and after 4h to 0.51 mm depth away from the meniscus.



**Figure 3.14.** Nugget position vs. the nugget number and size in 4 h heating experiments at 1300 °C and 1250 °C.

# **3.6.4.** Quench nugget formation

Our nugget locations and sizes allow us to also consider the quench nugget formation hypothesis. Cottrell and Walker (2006) proposed nugget formation due to saturation concentrations decreasing during cooling of the sample. At slight undercooling, 1300 °C to 1250 °C, we do not find that either the number of nuggets or their size increase. Additionally, nuggets are found only close to the meniscus and not randomly distributed throughout the samples or close to the bottom of the crucible, as one would expect if the nuggets were formed by cooling.

We can combine known geochemical data with diffusivity estimates to offer a simplistic calculation of the maximum size potential quench nuggets might reach. Since we know our samples contain ~ 6 ppm of Pt, we can calculate how much melt we would need to make nuggets of a certain size, using the Pt density of 21.4 g/cm<sup>3</sup> (Palache et al., 1944) and the calculated melt density of 2.66 g/cm<sup>3</sup> at 1300 °C (Lange and Carmichael, 1987; Ochs and Lange, 1997; Scilab script written by DRB). We can further estimate how much time it would take to form nuggets of a certain size if we know the diffusion coefficient. Unfortunately, diffusion coefficients for Pt in silicate melt are not reported. We can however make some estimations based on diffusivity of Si in basaltic melt (Lesher et al., 1996) of 8.45 x 10<sup>-12</sup> m<sup>2</sup>s<sup>-</sup> <sup>1</sup> and S (sulphur) diffusion in basaltic melt (Freda et al., 2005) of 1.2 x 10<sup>-11</sup> m<sup>2</sup>s<sup>-1</sup>, diffusion of Mn (Henderson et al., 1985) of 3.74 x  $10^{-11}$  m<sup>2</sup>s<sup>-1</sup> and Re diffusion of 3.16 x  $10^{-11}$  m<sup>2</sup>s<sup>-1</sup> (MacKenzie and Canil, 2008). By choosing Si, one of the most abundant elements in basaltic melt, we obtain a lower diffusivity estimate, as elements will usually not diffuse slower than the major component of the melt (Zhang, 2010). Pt is often associated with S, so it is chosen as well. Re diffusion, studied by MacKenzie and Canil has a similar value to Mn, but the experiments by MacKenzie and Canil show some variability so their values are compared to Mn. These are approximations and thus, in order to calculate the time required to form nuggets,
the half distance of diffusion equation is used  $x \approx \sqrt{Dt}$ . The diffusion is taken to be constant even though it will drop as the temperature drops by about an order of magnitude for every 200 °C (Lesher et al., 1996; Freda et al., 2005) and make the possible nuggets formed during quench even smaller. The largest nuggets that could be formed during quench given these approximations are smaller than 0.35 µm, as seen in Figure 3.14A, until the sample reaches the glass transition temperature of around 690 °C (Giordano et al., 2005). In Ertel et al. (1999) it is stated that nuggets smaller than 0.05 µm will not be noticeable in LA-ICP-MS analysis. Our calculations are most likely slightly overestimated, as we applied the same diffusion coefficient through all the temperatures. Nonetheless, even if the nuggets are formed during quench, they would not be noticeable by LA-ICP-MS.

Additionally, we calculate approximate nugget sizes that would be able to grow during the high-temperature step of the experiments (Fig. 3.15B). The maximum size of the nuggets that can grow during the experiment is 6  $\mu$ m, based on our approximation. Given the size overestimation while using X-ray  $\mu$ CT, if nuggets bigger than 8  $\mu$ m are excluded then our results show an even stronger bias towards formation in the range of lower *f*O<sub>2</sub> and appear to confirm the hypothesis by Bennett et al. (2014) of nuggets forming within previously oxidizing material at high temperature.



**Figure 3.15.** Size of possible nuggets given for a range of diffusion coefficients since the diffusion coefficients for Pt are unavailable. A) The size range possible for nuggets if they are formed at quench. B) The size range of nuggets that can be formed during the experiment.

#### **3.7.** Conclusions

- I. Nuggets formed in oxidizing conditions during sample preparation in air at 1300 °C. After heating to 1350 °C for 72h to remove the bubbles and before heating at the synchrotron the nuggets are all located within 0.54 mm of the meniscus. Since the meniscus bottom distance from the bottom of the crucible is on average more than 3 mm, we conclude that the nuggets are unevenly distributed through the samples, as the nuggets are all concentrated close to the meniscus. This strengthens the case of using X-ray μCT in investigating experimental samples as these nuggets could easily be missed. The unexpected nuggets at oxidizing conditions and the preferred location at the top of the crucible before introducing the fugacity gradient combined with the fact the nuggets should have sunk to the bottom of the crucible during the 72 h heating points to dynamic processes that require further real time studies.
- II. At temperatures higher than 1300 °C nuggets form close to the meniscus, within the  $fO_2$  gradient. At 1300 °C and 1250 °C there are more small nuggets close to the meniscus, but the results are not as conclusive as those for the higher temperatures.
- III. After shorter (1 h) heating there are fewer nuggets than before heating, indicating that it takes time for the fugacity gradient to take effect in the basaltic melt.
- IV. Using the known quench time, an approximate calculation can be made to show Pt nuggets are unlikely to form during the short quench time (50 s from 1400 °C to 630 °C) available. If they have formed, they would be less than 350 nm in length and they might not be detectable by LA-ICP-MS.

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## **CHAPTER 4**

# The formation and incorporation of laurite in chromitite layers of the Stillwater Complex – insights from X-ray imaging

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### 4.1. Rationale

In Chapter 4, we move our focus to natural samples enriched in PGE. I have chosen to study samples from chromitite layers from the lower Peridotite Zone of the Ultramafic Series of the Stillwater Complex (Montana, USA). Stillwater is one of the three main layered mafic intrusions hosting PGE ore deposits. I studied samples with known whole rock geochemistry and platinum-group mineral (PGM) distributions (determined in 2D).

I applied laboratory-based X-ray computed microtomography ( $\mu$ CT) to massive chromitite samples and obtained accurate volumes and locations of all phases, most importantly chromite and laurite. Laurite is the main Ru-host in these samples and how laurite forms has been significantly debated, as understanding laurite formation enhances our knowledge of PGE ore deposit formation. I compared  $\mu$ CT results to earlier studies of PGM location and textural relationships in 2D for the same sample set (Barnes et al., 2016; Prichard et al., 2017; Wavrant, 2017) and combined my textural findings with the whole rock geochemistry. This allowed me to perform mass balance and diffusion calculations, with the goal of examining the validity of several proposed laurite formation processes.

This chapter is being prepared for publication with M. Kudrna Prašek as a first author, in collaboration with Sarah-Jane Barnes, Don R. Baker, Lucia Mancini, Lucia Pappalardo and Pia Pleše.

#### 4.2. Abstract

In order to improve our understanding of where, when, and how platinum-group elements (PGE) are concentrated, detailed studies of the nature and textures of the minerals hosting the PGE are necessary. The PGE may be divided into those that behave in a compatible fashion (Os, Ir, Ru) known as the IPGE and those that are generally incompatible (Pt and Pd) (PPGE); the remaining PGE, Rh behaves in an intermediate fashion. The reasons for this difference in behavior is not clearly understood, but there are several processes (not necessarily exclusive) that could lead to fractionation of IPGE from Pt and Pd. The first is that the IPGE partition into the early crystallizing minerals, olivine and chromite. Natural chromites from volcanic rocks and subvolcanic sills support this argument, as does experimental work. However, massive chromitites from layered intrusions and podiform chromitites from ophiolites are particularly rich in IPGE relative to Pt and Pd, although chromite minerals contain no detectable IPGE. Laurite minerals [Ru(Os,Ir)S<sub>2</sub>] and IPGE alloys are commonly found within the chromite minerals. This could be because IPGE are less soluble in chromite than Pd and Pt, particularly under low  $fO_2$  conditions. Small (< 1 micron) laurites can be found at the interface between chromites and either glass or another mineral. Thus, laurite may crystallize at the same time as chromite and olivine. Post cumulus processes also need to be considered. Chromite minerals in massive chromitites consist of sintered crystals, and it has been suggested that initially the IPGE partition into chromite, but during post cumulus processes there is an exchange of IPGE and Fe and Ni between the chromite and interstitial base-metal-sulfides (BMS) crystals that convert the sulfides to laurite. The sintering of chromite leads to inclusion laurite in some cases. Finally, some workers suggest chromitite layers form as the result of melting orthopyroxene rich rocks by the introduction of a hydrous fluid. The Cr from these rocks form chromite. In this case, orthopyroxene rich rocks are thought to have contained a small amount of disseminated BMS, which largely dissolved in the hydrous

fluid, leaving laurite as a peritectic phase. The location and form of both the chromite and laurite could help constrain the origin of laurite. However, to date their distribution and size have mainly been studied in polished sections. Observations in 2D can be misleading as the size of the minerals tends to be underestimated and the relationships among mineral grains can be misinterpreted, as the third dimension is not visible.

We investigated six massive chromitites from the Stillwater Complex (Montana, USA) using laboratory-based X-ray computed microtomography ( $\mu$ CT). Fourteen laurites [Ru(Os,Ir)S<sub>2</sub>] were found, nine located within, and five located between chromites, indicating that chromite-hosted laurite dominates over interstitial laurite. Those included in chromite crystals are largely found towards the edge of the crystal. The volumes of all laurites varied from ~ 120 to ~ 2000  $\mu$ m<sup>3</sup> (greater than indicated by 2D studies). These laurites can account for the all the IPGE in the massive chromitites. For the laurites to have formed by direct crystallization they would have to have interacted with ~ 6 x 10<sup>8</sup> more silicate magma volume than the laurite volume. For the laurite to have formed by transformation of BMS sulfide to laurite the IPGE would have to have been collected from a few hundred chromites and 64 000 to 400 000 years would be needed to achieve the diffusion through multiple neighboring chromites. Our findings suggest that diffusion of Ru through chromites is a more probable mechanism of laurite formation.

Keywords: Stillwater, chromite, laurite, X-ray microtomography, Ru diffusion

#### **4.3. Introduction**

Platinum-group elements (PGE) are comprised of Pt, Pd, Rh, Ru, Os, Ir. They are commonly divided into the Ir-PGE (IPGE, comprising Ru, Os, Ir), which behave as compatible elements, and Pd-PGE (Pd and Pt), which behave as incompatible elements, while Rh behaves in an intermediate fashion (Barnes, 1999). The IPGE and in some cases Rh, are enriched relative to Pd and Pt in chromite-rich layers in layered intrusions and ophiolites (e.g., Pagé et al., 2012, and references therein; González-Jiménez et al., 2014; Osbahr et al., 2014; Pagé and Barnes, 2016; Barnes et al., 2016). The most common platinum group mineral in these chromite-rich rocks is laurite [Ru(Os,Ir)S<sub>2</sub>] and because Os isotopes in laurite are key to understanding mantle-derived melt differentiation (González-Jiménez et al., 2014), understanding how laurite forms is important for fundamental research. In addition, Os isotopes in laurites are also used to infer that PGE deposits and some nickel-sulfide deposits form from mafic magmas that have been contaminated by crustal rocks (Lambert et al., 1999; Horan et al., 2001; Keays and Lightfoot, 2004; Reisberg et al., 2011; Barnes and Ripley, 2016), thus understanding how laurite forms is also important to the formation of magmatic Ni and PGE ore deposits.

Numerous studies of sizes and textural relationships of platinum-group minerals (PGM) have been performed (e.g., O'Driscoll and González-Jiménez, 2016 and references therein). The texture (size, shape and the relationship with other minerals present in the rock) of PGM is important both from the point of view of petrogenesis and extractive metallurgy. In most cases, for petrological purposes, PGM have been studied in polished thin sections, however in the past 10 years two new techniques have been applied. First, hydro separation of PGM has been used (e.g., Good et al., 2017), where the true volume and shape of PGM can be measured, but textural information is lost. Secondly, PGM have been investigated by high-resolution X-ray computed tomography (e.g., down to 0.7 µm of effective pixel size in Godel, 2013), where

textural data and 3D measurements are obtained, however only a relatively small rock volume can be examined, in most cases  $< 1 \text{ cm}^3$ .

The processes responsible for IPGE fractionation from Pt and Pd remain poorly understood. IPGE might partition into olivine and chromite during early melt crystallization, however, whereas massive chromitites from layered intrusions and ophiolites are IPGE rich (relative to Pt and Pd), their constituent individual chromites have no detectable IPGE. The IPGE are instead present as laurite and IPGE alloys, both commonly found within and among the chromite and olivine. Potential post cumulus processes may have played a significant role in laurite formation, possibly IPGE that have initially partitioned into chromites (now sintered) underwent a diffusive exchange with Fe and Ni originating from an interstitial base-metalsulfide (BMS). The process would convert the BMS into laurite. As laurite is the principle IPGE host in massive chromitites, studying its location, size, and textural relation with chromites will help us understand IPGE fractionation processes.

Here I approached the question of how the PGM laurite forms by applying laboratorybased X-ray computed microtomography ( $\mu$ CT) to samples from chromitite layers of the Stillwater complex, Montana, USA. I compared our  $\mu$ CT results to multiple earlier studies of PGM location and textural relationships in polished thin sections of the same rock samples (Barnes et al., 2016; Prichard et al., 2017; Wavrant, 2017). I have found that laurites are mostly located within chromites and a few large laurites can account for the entire Ru budget of analyzed samples. Our 3D data allows a refinement of laurite-chromite and laurite-melt mass balance calculations, as well as time-resolved diffusion calculations for specific minerals.

## 4.4. Geology and stratigraphy of the Stillwater Complex

The Stillwater Complex (Montana, USA; Fig. 4.1) is a layered ultramafic-mafic intrusion, 5.3 km thick and 44 km long (Todd et al., 1982; Boudreau, 2016) that was emplaced

from 2712 to 2709 Ma (Wall et al., 2010; Wall et al., 2018) into regionally metamorphosed sedimentary rocks of the Wyoming Archean Province at 12 – 16 km depth (Thomson, 2008; Hanley et al., 2008). It was metamorphosed to greenschist facies at ~ 1700 Ma and water infiltrated into the complex (Nunes and Tilton, 1971; Nunes, 1981; Page, 1977), but the primary igneous mineralogy is mostly preserved (Jackson, 1961; Irvine et al., 1983; Boudreau, 2016). Only a short summary of the stratigraphy is presented below, and the reader is referred to Boudreau (2016) for an in-depth overview.

The Stillwater complex is divided into five series: Basal, Ultramafic, Lower Banded, Middle Banded, and Upper Banded series (Fig. 4.1, Zientek et al., 2002; Boudreau, 2016). The Ultramafic Series is further divided into the lower Peridotite Zone and the upper Bronzitite Zone (~ 500 and 200 m respective thickness, Raedeke, 1982; Raedeke and McCallum, 1984; Barnes et al., 2016; Jenkins and Mungall, 2018). The Peridotite Zone is a sequence of ~ 20 cyclic units of harzburgites ( $\pm$  chromitites), harzburgites, and (olivine) orthopyroxenites (Raedeke and McCallum, 1984), most likely emplaced as series of thin sills (based on age data from Wall et al., 2010; Wall et al., 2018).

Layers of semi-massive, massive, and disseminated chromitite are found near the base of ten out of 20 cyclic units of the Peridotite Zone (Jackson, 1969; Cooper, 1997; Zientek et al., 2002; Barnes et al., 2016; Boudreau, 2016). These chromitite layers are labeled A - K from the lower most layer (Fig. 4.1., Jones et al., 1960), and the IPGE and Rh are enriched in them relative to Pd and Pt and relative to the silicate rocks (Barnes et al., 2016).

The minerals hosting PGE in the Stillwater A-K chromitites are mainly PGM (Barnes et al., 2016). Among the latter, laurite is the principal IPGE host (Talkington and Lipin, 1986; Prichard et al., 2017). Thus, the processes responsible for laurite formation could be responsible for chromitite IPGE enrichment.



**Figure 4.1.** Map, stratigraphy and lithological details of chromite units at the Stillwater Complex. Modified after Boudreau (2016), and Barnes et al. (2016).

#### **4.5.** PGM in chromite-rich rocks – current formation models

At the  $fO_2$  conditions in the crust, platinum-group elements behave as chalcophile elements and form PGM, such as laurite (RuOsIr)S<sub>2</sub>. The enrichment of IPGE and Rh in chromite-rich rocks is common in ophiolites, zoned complexes and layered intrusions (Pagé et al., 2012; González-Jiménez et al., 2013; Barnes et al., 2016; Zaccarini et al., 2018), and laurite is commonly found in these chromite-rich rocks. Chromites from plutonic settings only contain a few ppb IPGE and Rh and the IPGE in these rocks are hosted in laurite (Pagé and Barnes, 2016; Park et al., 2017). In contrast, chromites from volcanic rocks contain hundreds of ppb IPGE and Rh (Park et al., 2012; Pagé et al., 2012; Kamenetsky et al., 2015; Pagé and Barnes, 2016; Arguin et al., 2016).

There are four main laurite formation models proposed, that focus on the following, mutually non-exclusive, processes: I) laurite crystallization from a BMS-undersaturated melt (e.g., Page, 1971; Prichard et al., 1981; Merkle, 1992; Peck et al., 1992; Prichard et al., 1994; Brenan and Andrews, 2001; Andrews and Brenan, 2002; Bockrath et al., 2004), II) laurite crystallization at the chromite-melt interface due to a decrease in  $fO_2$  (Finnigan et al., 2008), III) diffusive exchange of elements between IPGE-rich chromites and BMS, which converts the latter to laurite (Barnes et al., 2016; Pagé and Barnes, 2016), and IV) laurite crystallization from a residual melt after partial melting induced by a hydromagmatic fluid (Boudreau and Meurer, 1999; Boudreau, 2008; Veksler and Hou, 2020).

The first process is direct crystallization of laurite from a mafic melt, because the melt becomes saturated in laurite at lower  $fS_2$  than FeS (Melcher et al., 1997), i.e., before any other mineral or a Fe-Ni-Cu-sulfide liquid or a base-metal-sulfide liquid (Page, 1971; Prichard et al., 1981). Brenan and Andrews (2001) and Andrews and Brenan (2002) showed experimentally that laurite could crystallize from a mafic melt at crustal  $fO_2$  and  $fS_2$  conditions provided  $fS_2$  is not high enough to provoke BMS saturation. Euhedral laurites could afterwards become included in olivines or chromites, either at their edges or close to their center. The model however only works above 1200 °C, as below that temperature the melt becomes saturated in FeS liquid, which would dissolve most of the laurite (Bockrath et al., 2004) and does not explain the IPGE enrichment of massive chromitites (from both layered mafic intrusions and podifrom ophiolites) when compared to associated harzburgites or dunites.

The second process necessitates that chromite crystallization preceded laurite crystallization. Chromite crystallization from a mafic melt lowers the  $fO_2$  at the chromite-melt interface which induces laurite saturation (Capobianco et al., 1994; Finnigan et al., 2008). This would account for the enrichment of IPGE over Pd and Pt in the chromitite layers because laurite does not contain detectable Pd and Pt. According to Finnigan et al. (2008) laurite forms in the 20-µm thick chromite-melt boundary region (CMBR). This would produce very small laurites (< 0.5 µm, Finnigan et al., 2008). Some natural volcanic chromites exhibit such textures, e.g., Arguin et al. (2016). As in the case outlined above, this process also requires that the magma not be saturated in BMS liquid because BMS would dissolve up to weight percent levels of Ru and hence impede the crystallization of laurite (Andrews and Brenan, 2002). A weakness of this model is that in addition to the rare occurrence of nano-nuggets of laurite in at the margins of chromite mineral grains, chromites from volcanic rocks contain sufficient Os, Ir and Ru to account for the bulk of these elements in the rocks (Pagé and Barnes, 2016; Arguin et al., 2016).

The third process occurs post cumulus and considers possible mechanisms when basemetal-sulfides are present, as is the case in Stillwater (Page, 1971; Barnes et al., 2016; Wavrant, 2017). The Stillwater chromitite layers are enriched in IPGE and Rh, and they contain both BMS and laurites (Prichard et al., 2017; Wavrant, 2017). Contrary to the first process presented, where BMS are a hindrance for laurite crystallization, here BMS are crucial. Based on the difference between the high IPGE concentrations in volcanic chromites and low IPGE content of the plutonic chromites, Barnes et al. (2016) and Pagé and Barnes (2016) suggested that IPGE and Rh are initially incorporated into crystallizing chromite. Subsequently, the melt became saturated in BMS liquid, which percolated into the semi-consolidated layers of IPGE- and Rh-rich chromite (Fig. 4.2 A1 and A2). During the slow cooling of the plutonic rocks, the IPGE and Rh, which had originally partitioned into the chromite, convert most BMS into laurite by diffusive exchange of IPGE and Rh into the sulfide, and Ni and Fe out of the sulfide and into the chromite (Fig. 4.2 B1 and B2) and loss of S. The predicted laurite location would be either among several chromites or within chromites and close to their edges, due to chromite sintering (Fig. 4.2 C1 and C2).

The fourth process is also post cumulus and entails the addition of a fluid to a semiconsolidated pile of orthopyroxenite-norite cumulate (Mathez, 1995; Boudreau and Meurer, 1999; Boudreau, 2008). The orthopyroxenite then undergoes partial melting, forming a Crsupersaturated melt. Chromite crystallizes from said melt at the old norite-pyroxenite contact. This model addresses the problem of chromite-rich layer formation, as direct cotectic crystallization of chromite from a mafic melt would result in a cumulate with only 1 to 2 % chromite, due to the low  $Cr_2O_3$  concentrations of the magma (Irvine, 1967 and 1977; Zhou et al., 1994; Roeder et al., 2006). Veksler and Hou (2020) modeled the formation of the chromiterich layers in the Bushveld Complex (South Africa) whereby a norite cumulate undergoes hydrous melting. Their residuum would be sufficiently chromite-rich to form a chromitite layer. Laurite would also crystallize from this residual-chromite saturated melt, at the old norite-pyroxenite interface due to lower  $fO_2$  induced by the chromite crystallization. The predicted laurite location would be at the chromite-silicate interface.

In order to study how laurite forms it is critical to first correctly determine the laurite content and location in chromitites, as the second and fourth models predict laurites outside chromites but adjacent to them and the first and third models predict laurites within or between several chromites. To date, petrographic studies of laurites in chromitites were based on 2D methods (e.g., Prichard et al., 2008; Gonzalez-Jiménez et al., 2009; Osbahr et al., 2014; Prichard et al., 2017). Any 2D to 3D conversion on only a few samples may contain errors (Higgins, 2006), and possibly lead to underestimations of the laurite volume, and thus how much of the Ru, Os, Ir in the sample is controlled by laurite.



**Figure 4.2.** Illustration of Barnes et al.'s (2016) model for sulfide entrapment and enrichment in IPGE and Rh by diffusive replacement, with two possible entrapment scenarios. A1-C1 depicts the setting at a chromite-melt interface; A2-C2 depicts the setting between several chromites. A) Before entrapment, chromites (Chr, dark grey) are enriched in IPGE (Os, Ir, Ru) and Rh, while the base-metal-sulfide (BMS) is PGE (Pt, Pd, Rh, Ru, Os, Ir) rich. A1) at a single chromite-melt interface, A2) between several chromites. B) BMS entrapment, B1 via chromite growth, B2 via chromite sintering. IPGE and Rh diffuse into the sulfide and Ni and Fe diffuse out of the sulfide into the chromite. C) After a slow cooling, laurite is formed and the chromites are now IPGE-poor, in both settings C1 and C2.

#### 4.6. Materials and methods

Six samples were analyzed by laboratory-based X-ray µCT. They are labeled as follows: ST010B4, ST011G1, ST011G4, ST003H, ST014I and ST001J1 (from layers B, G H, I and J, respectively). These samples were selected from a larger study of the chromitite layers of the Stillwater Complex, which characterized the whole rock geochemistry and PGM distribution (Barnes et al., 2016; Prichard et al., 2017). The chromitite layers contain small but variable amounts of BMS. However, based on their mineralogy (Wavrant, 2017) and on S/Se ratios, all of the chromitite layers have lost S. In order to take account of the variable amounts of BMS originally present in the rock the samples were chosen based on their Pd/Ru ratio, where ST010B4 and ST001J1 have the highest Pd concentrations and the highest Pd/Ru ratio and hence the highest originally BMS content, and ST011G1 and ST011G4 have the lowest. Samples ST003H and ST014I have intermediate Pd concentrations and Pd/Ru ratios. In addition, our sample selection covers a wide section of the stratigraphy (layers B to J) and contains laurites large enough (> 10  $\mu$ m<sup>3</sup>) to be detected by the X-ray  $\mu$ CT experimental setup (based on previous 2D analysis, Prichard et al., 2017). The X-ray µCT technique was chosen to precisely quantify the number, volume and placement of potential PGM within the investigated sample volume. A scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) study of two samples was conducted to confirm the identity of the PGM and/or PGE found by µCT.

## 4.6.1. Sample characteristics

The samples investigated were drilled cores of ~ 2 mm diameter and heights of 5 to 10 mm. All samples in this study are pieces of the previously analyzed rocks (Pagé and Barnes, 2016; Barnes et al., 2016) composed of 0.2 to 2 mm chromites and interstitial olivine and orthopyroxene, along with laurite  $(1 - 5 \mu m)$  and pentlandite (Fe,Ni)<sub>9</sub>S<sub>8</sub>), millerite (NiS),

malanite (Cu-Pt-RhS) and chalcopyrite (CuFeS<sub>2</sub>), with the latter four 0.01 – 0.1 mm in size, (Barnes et al., 2016; Prichard et al., 2017; Wavrant, 2017). A summary of previously reported PGM and PGE alloys in Stillwater samples from these chromitite layers is given in Table 4.1. These observations were made by scanning electron microscopy and X-ray fluorescence in Barnes et al. (2016), by scanning electron microscopy energy-dipsersive X-ray analysis in Prichard et al. (2017), and by scanning electron microscopy and electron microprobe analysis in Wavrant (2017).

**Table 4.1.** Summary of results from previous 2D studies (see text) of platinum-group minerals (PGM) of the Stillwater samples analyzed in this study (Prichard et al., 2017; Wavrant, 2017). N = number, BMS = base-metal-sulfide, Rt = rutile, NiS = millerite. The minimum (min) and maximum (max) axes were obtained through 2D measurements on polished sections.

	Mineral	Location	Min axis	Max axis		Associated	
Sample			(µm)	(µm)	N <sub>mineral</sub>	minerals	
ST001J1	Laurite	within chromite	4.7	11.3	4	BMS/PdPGM	
	PdPb	between chromites	0.3	3	4	BMS	
ST014I	Laurite	within chromite	1.7	7.4	6	Silicates/BMS/Rt	
	Laurite	between chromites	1	1	2	BMS/PdPtPGM	
	Pd alloy	between chromites	1	3	2	BMS	
	Pt alloy	between chromites	5	6	2	BMS	
ST003H	Laurite	within chromite	2.8	7	10	Silicates	
	Laurite	between chromites	3	6	1	BMS	
	PdTe	between chromites	1	4	2	BMS	
ST011G4	Laurite	within chromite	2	4.7	6	Silicates	
ST011G1	Laurite	within chromite	2.2	6.4	6	NiS/Silicates	
	Laurite	between chromites	9	9	1	BMS	
ST010B4	Laurite	within chromite	2.8	6.7	2	PtPd PGM	

## 4.6.2. X-ray µCT imaging

X-ray µCT imaging was performed at the Istituto Nazionale di Geofisica e Vulcanologia (INGV) of Napoli (Italy) using a ZEISS XRadia 410 Versa X-ray microscope, coupled with a 2k x 2k pixels, low noise charge-coupled detector. The scanning parameters are summarized in Table 4.2. A single region per sample was scanned, during continuous sample rotation (total scanning angle of 360°), in the region-of-interest mode. The choice of filter (air, i.e., no filter, or high energy) depended on transmission values and was chosen based on ZEISS protocols. The 2D radiograms produced by each µCT scan were reconstructed into 3D volumes using the Standard Analytical Reconstruction software (based on the FDK algorithm, Feldkamp et al., 1984, provided by ZEISS with the instrument) and the final reconstructed images were delivered in .tiff format. The beam hardening correction was performed using the ZEISS XRM Reconstruction software. No streak metal artefacts were observed. All samples were scanned using 10x magnification, but a small volume in sample ST014I was scanned at 20x magnification (Table 4.2) to obtain a more accurate volume of an identified object of interest. An isotropic voxel size ranging between 2.08 and 2.25 µm for 10x magnification, and 1.12 µm for 20x magnification, was used for reconstruction (Table 4.2). Entire reconstructed 3D volumes (~  $10 \text{ mm}^3$ ) were used for analysis.

Sample	ST010B4	ST011G1	ST011G4	ST003H	ST014I		ST001J1
Source-to-sample distance (mm)	25.5	28	27	28	25.5	25.5	27
Sample-to- detector distance (mm)	7.5	7	6	7	5	5	7
Voltage (kV)	130	120	100	100	130	150	100
Power (W)	10	10	10	10	10	10	10
Microscope objective	10x	10x	10x	10x	10x	20x	10x
Filter	air	HE1	air	HE1	air	air	HE1
Pixel binning	2x2	2x2	2x2	2x2	2x2	2x2	2x2
Exposure time/projection (s)	1.5	2.8	2.1	3.4	1.4	8	3.2
Side of the square FOV (µm)	2092	2162	2212	2162	2260	1115	2147
Effective pixel size (µm)	2.08	2.15	2.20	2.15	2.24	1.12	2.13
# of projections	4001	4001	4001	4001	4001	4001	4001

**Table 4.2.** Summary of X-ray microtomographic scanning conditions. FOV = field of view, HE = high energy, # = number. The total scanning angle for all samples was 360°.

## 4.6.3. X-ray µCT data processing and analysis

Morphological analysis on binarized volumes of (suspected) laurite, chromite and silicates was performed using the *Pore3D* software library (Brun et al., 2010). Subvolumes were used only for visualization purposes. The 3D visualization was obtained using the software package Avizo Fire® (Visualization Sciences Group).

X-ray µCT in absorption mode provides a map of the linear attenuation of X-rays passing through an object, and their attenuation partly depends on the density of phases present in the object, in our case minerals in a rock (Baruchel et al., 2000). To simplify, we can say minerals are distinguished as separate phases due to their density differences. Laurite has a higher density (6.43 g/cm<sup>3</sup>, Bowles et al., 1983) than chromite (4.5 g/cm<sup>3</sup>; Palache et al., 1944), BMS (from 4.2 g/cm<sup>3</sup> for chalcopyrite to 4.8 g/cm<sup>3</sup> for pentlandite; Palache et al., 1944) or silicates (Mg-olivine 3.2 g/cm<sup>3</sup> and Mg-orthopyroxene ~3.5 g/cm<sup>3</sup>; Dana, 1892). Other PGM and PGE-alloys have been reported in these rocks (Table 4.1), e.g., Pd- and Pt-alloys with densities > 15 g/cm<sup>3</sup> (Lide, 2004), located between chromites (Wavrant, 2017; Prichard et al., 2017). Laurite is the least dense among them, however these PGM and PGE-alloys are often found together (e.g., see Fig. 5 in Barnes et al., 2016, Fig. 3 in Prichard et al., 2017 and Fig. 2.8 in Wavrant, 2017), and such an assemblage has high X-ray attenuation coefficients, at energies > 100 keV (Godel, 2013), too close to differentiate between PGM and PGE-alloys in laboratory-based X-ray µCT experiments in absorption mode. In order to identify the high density objects in the samples, knowledge of mineralogy and SEM imaging are necessary, to complement microtomographic data.

The suspected laurites are very small (only a few micrometers in size, Barnes et al., 2016), potentially smaller than our best spatial resolution, which poses a significant challenge for the analysis of X-ray  $\mu$ CT images. To counter this effect, special attention was required during thresholding, which was performed on 16-bit instead of 8-bit images.

#### 16-bit vs. 8-bit conversion of the reconstructed slices

In this study, we found that reconstructed volumes in 16-bit format allowed more accurate thresholding of the phases of interest (suspected laurites). A conversion from 16-bit to 8-bit images is convenient in terms of computational power and memory allocation; however, the use of 16-bit images is important to retain the full information provided by the 16-bit detector employed.

The differences between 16- and 8 bit images are displayed in Figure 4.3 where 16-bit (A, C) and 8-bit (B, D) images of two axial slices (A, B vs. C, D) from sample ST011G4 are compared. The exact threshold values we report in this section are for sample ST011G4, for other samples they are similar. Two objects of interest (a smaller,  $1.84 \times 10^3 \mu m^3$ , in panels A and B and a larger,  $43.5 \times 10^3 \mu m^3$ , in panels C and D) are found about 425 microns vertically apart. The first (A, B) appears to be a laurite, due to the high absorption (confirmed by SEM in the following section). Using the grey-scale threshold of 60025 in Fig. 4.3.A, the object is selected (colored in red). Thresholding is an image segmentation method where binary images are created out of greyscale ones and the binary value of 1 is assigned to the phase we wish to segment out, here suspected laurites. To threshold the same object in the 8-bit image of the same virtual  $\mu$ CT section, a threshold of 245 is applied (Fig. 4.3.B, object is again in red).

For 8-bit images to adequately represent the 16-bit ones, the threshold of 245 in 8-bit images and the threshold of 60025 in 16-bit images should select the same objects throughout the sample. Thus, in order to verify the validity of using the selected 245 threshold in the 8-bit image, the entire imaged volumes in both 16- and 8-bit versions must be compared one to the other, i.e., since the first object necessitated a 245 threshold in 8-bit to match the volume selected using the 60025 threshold in 16-bit (1.8 x  $10^3 \mu m^3$ ), this should hold for all such objects. Upon locating the larger (43.5 x  $10^3 \mu m^3$ ) object in both 16- and 8-bit images (Fig. 4.3C and D, respectively) and applying 60025 and 245 thresholds, respectively, we see

however that the same object is not segmented (not colored red) in the 16-bit image. Consequently, using 8-bit images would overestimate the total laurite volume. The non-segmented object in this case could be a different sulfide, as its brightness, and thus its density is lower than that of laurite (e.g., millerite, whose density of ~ 5.4 g/cm<sup>3</sup>, Palache et al., 1944, is between those of chromite and laurite), but we cannot ascertain which phase it may be from  $\mu$ CT data alone.



**Figure 4.3.** Comparison of thresholding in 16-bit (A, C) and 8-bit (B, D) reconstructed axial slices of sample ST011G4. Two features of interest (one in panels A and B and another in panels C and D) are found in sample ST011G4. A) Using the threshold of 60025 in a 16-bit image, the first feature is selected (colored in red). B) To select the same volume, a 245 threshold is applied in the 8-bit image. C) The 60025 threshold in the 16-bit image has not segmented the second, larger, feature (not colored in red). D) The 245 threshold in the 8-bit image has segmented the second feature (colored in red).

#### Thresholding high-density phases and chromites

Laurites are a high-density material (6.43 g/cm<sup>3</sup>) and thus strongly absorb X-rays, so they appear as bright voxels in the  $\mu$ CT reconstructed images and will often obscure the material in their immediate vicinity (Baruchel et al., 2000). In the reconstructed images, highdensity phases appear to have a bright halo that bleeds out into the lower-density material around them, such as chromite and BMS (both ~ 4.5 g/cm<sup>3</sup>) and silicates (~ 3.3 g/cm<sup>3</sup>), which may lead to an overestimation of the phase volume. Additionally, even though all laurites will have a very similar density (in the margins of their geochemical compositional variability, e.g., Ru content), due to different scanning conditions for each sample (Table 4.2) and differences in reconstruction and brightness/contrast adjustments prior to segmentation for each sample, the same thresholding value cannot be used across all samples. Consequently, conservative grey-scale thresholds of ~ 60 k - 65 k across all samples for 16-bit images were used to segment potential laurites (each sample, i.e., scan, with its own unique threshold value). Object borders, where the greyscale value was lower due to the halo effect, were also excluded (for all selected objects) leading to the thresholded volumes that represent the minimal possible object volume.

After thresholding, the sample volumes contained only binarized objects identified as potential laurites by their high absorption (which were later confirmed by SEM-EDS, see below). The smallest potential laurite was composed of 1 voxel ( $10 \ \mu m^3$ ) and the largest of ~ 780 voxels ( $7.5 \ x \ 10^3 \ \mu m^3$ ). Since our aim was to quantify the laurites that would significantly affect the rock composition, and not to overestimate their number in the rock sample, ~  $40 \ \mu m^3$  were used as the minimum volume of a laurite. We tested our approach by comparing total laurite volumes in a sample, with, and without, the ~  $20 \ \mu m^3$  and ~  $30 \ \mu m^3$  objects. If objects  $\leq 20 \ \mu m^3$  are removed, the total laurite volume lost is 0.3 % and if objects  $\leq 30 \ \mu m^3$  are removed, 0.4 % of the total laurite volume is lost. Thus the  $30 \ \mu m^3$  objects and smaller were excluded to reduce noise in the total sample volume and to keep a conservative approach. The

volumes of other Pd- and Pt-alloys (Table 4.1), are extremely small (~  $0.5 - 5 \mu m^3$ , calculated from 2D data; Wavrant, 2017; Prichard et al., 2017) and so they are either segmented along with laurites or fall into the 0.4 % of lost volume. One object with variable greyscale values (55 k - 65 k) in the 20x magnification scan of sample ST014I, a suspected high-density alloy aggregate, was not selected.

We used the volume of this suspected PGE-alloy aggregate to estimate the volume uncertainty. The 20x magnification yielded a 4 % larger volume,  $54.4 \times 10^3 \,\mu\text{m}^3$ , than at 10x magnification,  $52.3 \times 10^3 \,\mu\text{m}^3$ . Thus, we can provide a rough error of a 4 % volume underestimation. However, since this error estimate is based on only one object, we have neither included it in volume reports (Table 4.3), nor applied it to mass balance and diffusion calculations that treat with individual laurite volumes (section 4.8.3.). However, when we calculate the total laurite volume in a sample, for comparison between  $\mu$ CT and geochemical whole rock analyses of Ru in section 4.8.2., we examine the total volume with and without accounting for the 4 % volume underestimation.

Chromites were also segmented via thresholding to obtain the number of chromite crystals, their individual volumes, and the total chromite volume in a sample. In samples with closely packed, touching phases of the same density (e.g., Fig. 4.3, Fig. 4.5 and 4.6), separating individual mineral grains is challenging (Proussevitch and Sahagian, 2001). To count the chromites we employed a series of 3D filters to smooth the images, and we segmented chromites. Subsequently, an object separation using a 3D watershed filter (Ollion et al., 2013) was employed, followed by a 3D object counter (Bolte and Cordelières, 2006). The number of chromites counted is overestimated as multiple fractures divide chromite crystals (Fig. 4.3) and consequently their individual volumes are underestimated. Thus, the reported values of chromite crystal number and size are only a rough estimate, but the total volume of chromite is correct to within 1 x  $10^8 \mu m^3$  (the average sample volume is ~ 6 x  $10^9 \mu m^3$ ; Table 4.4). To

minimize the uncertainty associated with chromite volumes, we manually segmented each chromite that contained a suspected laurite (nine in total, e.g., Fig 4.5A, 4.6A, and 4.7D) because a correct host chromite volume is critical for mass balance and diffusion calculations presented in section 4.8.

As chromites and silicates are the two major phases in the investigated samples, they limit each other's thresholds, i.e., the chromite threshold value limits the silicate threshold value, so there is no volume overlap by assigning one voxel to two phases and thus counting it twice. This is why the standard deviations for chromite and silicate volumes per sample, reported in Table 4.4, are the same for both phases.

#### 4.6.4. SEM analysis

After the 3D distribution of possible laurites was determined by X-ray  $\mu$ CT, samples were manually sectioned to the position of the suspected laurites and polished for SEM analysis. Although straightforward in principle, polishing a sample until the desired micrometer-sized laurite target is exposed proved technically challenging. The grinding and polishing process necessitated continuous (every few microns) comparison of the polished sample with its original 3D volume to establish the location of the polished cross-section. This was performed until the potential laurite was reached. However, the laurites are small and even the gentlest polishing stroke removes a layer of at least a few microns. Of the six samples investigated, in only one sample was a potential laurite successfully retained, whereas in the others the potential laurites were either missed by over-polishing, or in one case plucked from the sample and lost.

The SEM images were acquired at the McGill University (Montréal, Canada). The two natural samples in question (one piece of ST003H with the exposed laurite and one piece of ST011G4 chromite, where the potential laurite was plucked during polishing) were analyzed using a Hitachi SU5000 Schottky Field Emission scanning electron microscope equipped with an Oxford X-MAX80 EDS detector with a 15 kV accelerating potential and 0.134 mA beam current. The sole purpose of the SEM analysis on the natural sample was to determine whether it is a laurite, and not to quantitatively characterize it further, as in Prichard et al. (2017).

4.7. Results

#### 4.7.1. X-ray µCT characterization of the Stillwater chromites

X-ray  $\mu$ CT images show the presence of silicates, chromites, and separate high-density objects. Based on the known mineralogical composition (Table 4.2, Barnes et al., 2016; Prichard et al., 2017; Wavrant, 2017), we assume that the highest density objects are PGM and PGE-alloys because these are the highest density (6.43 g/cm<sup>3</sup> and > 15 g/cm<sup>3</sup>, respectively) minerals in the samples investigated.

After thresholding and removal of objects  $\leq 30 \ \mu\text{m}^3$ , fourteen possible PGM or PGEalloys were found in the six scanned samples (Table 4.2). The minimum axis length was 2.13 - 2.15  $\mu$ m (one pixel edge, depending on the resolution, Table 4.2). The maximum axis length was ~ 35  $\mu$ m. Their volumes range from 0.05 x 10<sup>3</sup>  $\mu$ m<sup>3</sup> to 7.5 x 10<sup>3</sup>  $\mu$ m<sup>3</sup>, with an average of 1.22 x 10<sup>3</sup>  $\mu$ m<sup>3</sup> (Table 4.3).

Nine of the fourteen possible PGM or PGE-alloys were imaged within single chromites (Table 4.3, Figs. 4.6 – 4.8). They are always close to the chromite-silicate interface, 20-30  $\mu$ m away. The remaining five were imaged as interstitial phases. Four of these five were completely surrounded by chromites (two between two chromites and two at triple junctions of chromites) and one was in contact with both chromites and silicate minerals. The average volume of PGM or PGE-alloys within chromites is 0.62 x 10<sup>3</sup>  $\mu$ m<sup>3</sup> (ranging from 0.12 x 10<sup>3</sup> to 1.96 x 10<sup>3</sup>  $\mu$ m<sup>3</sup>; and those between chromites is 2.29 x 10<sup>3</sup>  $\mu$ m<sup>3</sup> (ranging from 0.05 x 10<sup>3</sup> to 7.54 x 10<sup>3</sup>  $\mu$ m<sup>3</sup>;
Table 4.3). Smaller PGM may exist in the samples, but were not detected with our  $\mu$ CT spatial and contrast resolution and because of our exclusion of volumes  $\leq 30 \ \mu\text{m}^3$ . There are no perceivable morphological differences between PGM within and between chromites. There is no correlation between the volume or shape of PGM (Fig. 4.8) and their location with respect to chromites. Although laurite is a cubic mineral, an ellipsoid was found to be a better descriptor of the segmented objects than a cube. Using a 3D ellipsoid, the average aspect ratio of all our PGM is 1:2:6 ratio (with the y axis obtained from  $= \frac{3V}{4\pi xz}$ , Harris and Stöcker, 1998), where V is the volume of the ellipsoid ( $\mu$ m<sup>3</sup>), x is the maximum axis, and z the minimum (in  $\mu$ m).

**Table 4.3.** (following page) Selected morphological parameters and location (marked with X) of the possible PGM and/or PGE-alloys from all samples. N = number.  $\overline{V}$  = average volume,  $V_{min}$  = minimum volume,  $V_{max}$  = maximum volume, all in  $\mu$ m<sup>3</sup>. For the position of layers B-J refer to Figure 4.1. The PGM analyzed by SEM is the largest among the five reported in sample ST003H.

			possibl	le PGM and/oi	r PGE-alloys		
Samples	N	Min	Max	Volume	Location		
Sampies		axis	axis	( <sup>3</sup> )	Within	Between	
		(µm)	(µm)	(µm <sup>*</sup> )	chromites	chromites	
		10.27	34.94	7.54 x 10 <sup>3</sup>		X	
ST001 I1	4	2.13	10.34	0.21 x 10 <sup>3</sup>	Х		
5100131	+	2.13	8.15	$0.12 \ge 10^3$	Х		
		2.13	8.62	0.13 x 10 <sup>3</sup>	Х		
STA1/I	C	5.10	16.50	$0.68 \ge 10^3$	Х		
510141	Z	2.25	11.50	0.35 x 10 <sup>3</sup>	Х		
		2.15	10.13	0.27 x 10 <sup>3</sup>	Х		
		2.15	5.60	$0.05 \ge 10^3$		Х	
ST003H	5	8.86	19.02	1.96 x 10 <sup>3</sup>	Х		
		2.15	10.23	0.25 x 10 <sup>3</sup>	Х		
		2.15	12.20	0.19 x 10 <sup>3</sup>		Х	
ST011G4	1	10.34	21.09	1.84 x 10 <sup>3</sup>		Х	
ST011G1	1	4.46	23.92	1.84 x 10 <sup>3</sup>		Х	
ST010B4	1	8.40	23.15	1.84 x 10 <sup>3</sup>	Х		
Average	2.3	4.62	15.38	1.22 x 10 <sup>3</sup>	Ī	7	
					$0.62 \ge 10^3$	$2.29 \times 10^3$	
Median	1.5	2.2	11.85	0.31 x 10 <sup>3</sup>	$0.27 \ge 10^3$	1.84 x 10 <sup>3</sup>	
Min	1	2.13	5.60	$0.05 \ge 10^3$	V	min	
					$0.10 \ge 10^3$	$0.05 \ge 10^3$	
Max	5	10.34	34.94	7.54 x 10 <sup>3</sup>	V	max	
	5	10101			$1.96 \ge 10^3$	7.54 x 10 <sup>3</sup>	
ST003H SEM		5.50	9.50				

We compared our volumes to those we converted from 2D data measured by Prichard et al. (2017) for each chromitite layer investigated (Fig. 2.4). In order to recalculate Prichard et al.'s (2017) data to 3D volumes we assumed each crystal had an ellipsoidal shape ( $V = \frac{4}{3} * \pi * x * y * z$ ; Harris and Stöcker, 1998), where y is the intermediate axis (in µm). As Prichard et al. (2017) only reported the length and width (x and z), we assumed an intermediate axis length (y) as the median value between the other two. We measured eight volumes smaller than those recalculated from Prichard et al. (2017), four in layer H, one in layer I and three in layer J (Table 4.3, Fig. 4.4), but our measured volumes in layer H are similar to those of Prichard et al. (2017) e.g., our measurement of 269 µm<sup>3</sup> compared to theirs of 280 µm<sup>3</sup>. We measured six PGM larger than those converted from Prichard et al. (2017), one in layers B, H, J and two in layer G (Table 4.3, Fig. 4.4). However, for these samples the volume difference between our study and Prichard et al. (2017) is considerable, varying from 7x in layer H to 18x in layer J.

The PGM diameters differ between the measurements of Prichard et al. (2017) and this study. Prichard et al.'s (2017) average 2D diameter is ~ 8 µm and our average 3D diameter is 11 µm (data obtained from volumes in Table 4.3 and Supplementary material 4.1, calculated as equivalent sphere radii;  $r = \sqrt[3]{\frac{3V}{4\pi}}$ , Harris and Stöcker, 1998).



**Figure 4.4.** Platinum-group mineral (PGM) volume comparison in each chromitite layer. Individual layers are shown on the x-axis and PGM volume ( $\mu$ m<sup>3</sup>) is on the y-axis. Volumes from this study (located either within chromites or between chromites) are single measurement values, volumes from Prichard et al. (2017) are layer averages from multiple laurites (data in Supplementary material 4.1). Prichard et al.'s (2017) volumes were obtained through 2D to 3D conversion assuming an ellipsoidal mineral shape.

Chromites were also segmented in each sample and their total volume and a rough estimate of their numbers (see section 4.6.3.) were obtained (Table 4.4). The total chromite volume ranges from  $3.14 \times 10^9 \,\mu\text{m}^3$  to  $5.81 \times 10^9 \,\mu\text{m}^3$  (for measurements of select individual chromite minerals see Table 4.9). The average individual chromite volume across all samples is  $5.02 \times 10^6 \,\mu\text{m}^3$  (Table 4.4). The volume fraction of chromite in the sample (volume of chromites divided by the sample volume) ranges from 0.55 for sample ST010B4 to 0.89 for sample ST001J1. The volume fraction of silicates (volume of silicates divided by the sample volume) ranges from 0.11 for samples ST011G1 and ST001J1 and 0.45 for sample ST010B4 (Table 4.4). The silicates are mainly olivines and orthopyroxenes (Barnes et al., 2016 and references therein).

The ratio of laurite to chromite crystals is smallest in sample ST001J1, 1:206, and highest in sample ST011G4, 1:1923. However, the high chromite count in sample ST011G4 is overestimated due to multiple fractures present in the sample. The average laurite to chromite ratio across all layers is  $\sim$  1:460.

**Table 4.4.** Measured volumes of silicate and chromite phases in the investigated samples. For chromites, their number and average volume is also reported. V = volume in  $\mu$ m<sup>3</sup>,  $\overline{V}$  = average volume in  $\mu$ m<sup>3</sup>, Vol. = volume, N = number, sd = standard deviation in  $\mu$ m<sup>3</sup>.

	V <sup>total</sup>		silicates		Chromites				
Samples	(x 10 <sup>9</sup> μm <sup>3</sup> )	V <sup>total</sup> silicate (x 10 <sup>9</sup> µm <sup>3</sup> )	sd (x 10 <sup>8</sup> )	Vol. ratio (φ)	V <sup>total</sup> (x 10 <sup>9</sup> µm <sup>3</sup> )	sd (x 10 <sup>8</sup> )	Vol. ratio	N	<i>V</i> individual chromite (x 10 <sup>6</sup> μm <sup>3</sup> )
ST001J1	6.40	0.69	0.12	0.11	5.72	0.14	0.89	825	6.04
ST014I	4.80	1.19	0.95	0.25	3.62	0.95	0.75	682	4.35
ST003H	6.50	1.39	1.77	0.21	5.16	1.77	0.79	975	4.71
ST011G4	7.00	2.50	1.06	0.36	4.48	0.99	0.64	1923	2.13
ST011G1	6.60	0.74	0.42	0.11	5.81	0.42	0.88	684	7.85
ST010B4	5.80	2.62	1.70	0.45	3.14	1.70	0.55	1264	2.06
Average	6.18	1.52		0.25	4.65		0.75	1059	5.02
Median	6.45	1.29		0.23	4.82		0.77	900	4.53
Min	4.80	1.19		0.11	3.14		0.55	682	2.06
Max	7.00	0.74		0.45	5.81		0.89	1923	7.85



**Figure 4.5.** 2D axial slices of samples A) ST010B4 and B) ST001J1 (isotropic voxel size =  $2.08 \mu \text{m}$  and  $2.13 \mu \text{m}$ , respectively) containing PGM, possibly laurite, imaged by X-ray  $\mu$ CT. Silicate minerals correspond to dark grey features, chromites to light grey, and PGM to white ones. A) The PGM is located completely within a chromite, but is close to the chromite-silicate interface (distance is  $20 \mu \text{m}$ ). Panel A corresponds to the scenario shown in panels A1-C1 in Figure 4.2. B) The PGM is located between several chromites. Panel B corresponds to the scenario A2-C2 in Figure 4.2.



**Figure 4.6.** The laurite in sample ST003H imaged by X-ray  $\mu$ CT and by SEM. A) 2D axial slice reconstructed by X-ray  $\mu$ CT and containing a laurite (isotropic voxel size size = 2.15  $\mu$ m). The laurite is 30  $\mu$ m from the chromite-silicate interface. B) SEM image corresponding to the axial slice presented in A. C) SEM image of a laurite (corresponding to the enlarged region of image B enclosed in a rectangle).



**Figure 4.7.** 3D visualization of sample ST003H, showing chromites, silicates and a laurite (isotropic voxel size =  $2.15 \mu$ m). A) Volume rendering of the chromites, shown in dark grey. The smaller white cube indicates the location of the subvolume depicted in panel C. B) Volume rendering of the silicates, shown in orange. C) Enlarged view of the subvolume shown in panel A, with a single chosen chromite shown in green. D) Isosurface rendering showing the shape of the chromite visible in C. The chromite has a volume of 0.14 mm<sup>3</sup>. E) Transparent view of the chromite presented in D; the location of the laurite within its volume is indicated with a white circle. F) Enlarged view of the laurite (volume =  $1.96 \times 10^3 \mu$ m<sup>3</sup>), shown in yellow.



**Figure 4.8.** 3D visualizations of ten selected laurites across all six samples. The laurites are from: A) sample ST010B4, B) sample ST011G1, C) ST011G4, D- E) sample ST014I, F) sample ST001J1, and G-J) sample ST003H. The values of the isotropic voxel size can be found in Table 4.2.

# 4.7.2. SEM analysis of natural samples

Only sample ST003H was successfully sectioned to the targeted high-density phase location (Fig. 4.7) and SEM analysis revealed the high-density phase is a laurite (composition given in Table 4.5). The purpose of the SEM analysis was only to confirm it is a laurite, as detailed 2D measurements and compositions of laurite in these samples are presented in Prichard et al. (2017). Our result nonetheless aligns well with Prichard et al.'s (2017) laurite compositions for layer H. This observation supports the use of thresholding values ~ 60k - 65k to separate laurite in the X-ray  $\mu$ CT reconstructions (Fig. 4.6 and 4.7).

**Table 4.5.** SEM-EDS semi-quantitative analysis of the sectioned laurite from sample ST003H (Fig. 4.7). Wt. % = weight percent, sd = standard deviation. Normalized average from three spectra. Exact spectra and their location can be found in Supplementary material 4.2.

Element	Wt. %	sd
Ir	4.74	0.02
Os	8.56	0.23
Ru	47.67	2.23
S	39.05	1.01
Total	100.00	

# 4.8. Discussion

Although several PGM and PGE-alloys are present (Table 4.1) in the Stillwater Intrusion, laurite is by far the most common, comprising ~ 90 % of all PGM inclusions and ~ 40 % of all interstitial PGM (Talkington and Lipin, 1986; Barnes et al., 2016; Prichard et al., 2017; Wavrant, 2017). Our SEM analysis indicated that the single PGM recovered within a chromite is a laurite as well. Hereafter we label all identified high-density objects as laurites (further reasoning is elaborated in section 4.8.2.).

In contrast to Prichard et al. (2017), the laurites found between chromites are larger than those within them (average volumes of 2.29 x  $10^3 \,\mu\text{m}^3$  and 0.62 x  $10^3 \,\mu\text{m}^3$ , respectively, Table 4.3), but our small number of identified laurites (n = 14) makes this observation inconclusive. Using high-resolution X-ray  $\mu$ CT we measured laurite volumes as small as those of Prichard et al. (2017) but we also identified larger laurites (Table 4.3, Fig. 4.4), some almost 20 times larger (e.g., in layer J, Fig. 4.4).

We discuss the following topics in the subsequent sections:

- 4.8.1. Comparison of our measured volumes and locations to previously published 2D data
- 4.8.2. The whole rock IPGE sample budget favors PGM identification as laurite
- 4.8.3. Origin of laurites associated with chromites, including:
  - Crystallization of laurites from a silicate melt necessary melt volumes and chromitite layer melt percolation times
  - Formation of laurite within chromite and the chromite volume needed for the observed laurites
  - Diffusion of Ru through chromite using diffusivity and volume constraints

# 4.8.1. Comparison of laurite dimensions measured by X-ray μCT with previous 2D measurements

In our 3D study, the laurite location is unambiguous. We found 9 laurites within chromites and 5 between chromites (Fig. 4.5). This result is in line with previous studies (Prichard et al., 2017; Wavrant, 2017) where more PGM were found within chromites than among them (144 vs. 57, respectively).

Prichard et al.'s (2017) SEM study reports 2D diameters of laurite that are smaller than the 3D diameters measured here (averages ca. 8 µm vs. ca. 11 µm, respectively), even though 2D methods are more likely to miss smaller grains than larger ones, due to not observing the entire sample volume (Higgins, 1994; Hoshide et al., 2006). Our potential underreporting of small volumes might be due to the imaging resolution we used, because the X-ray  $\mu$ CT resolution is insufficient to image laurites smaller than 10  $\mu$ m<sup>3</sup>. Additionally, the smaller 2D diameters observed by Prichard et al. (2017), compared to our 3D ones, may be due to the random nature of 2D sectioning. Obtaining the maximum cross section of a mineral from an infinity of possible cross-sections, i.e.,  $1/\infty$ , is undefined and can be considered as zero (Evans and Rosenthal, 2004). If we assume a 3D ellipsoid with x:y:z axes ratios of 1:2:5 (closest to our PGM ratio of 1:2:6, Table 4.3) belonging to the largest geometric class size, the probability of finding the maximum cross section increases to 1.76 % (Sahagian and Proussevitch, 1998, their Table 3). Consequently, 2D laurites will appear smaller than they are. This is further illustrated by the one laurite successfully sectioned here (Fig. 4.7) which is at least 10 µm across in the BSE-SEM image whereas analysis by X-ray µCT images of the same mineral grain produced a maximum axis of ca. 19 µm (Table 4.3). If the smaller laurite is used to estimate IPGE + Rh contents in the whole rock, the amount of IPGE + Rh hosted by laurite will be underestimated.

This point may be illustrated by comparing the actual volumes in this study, determined by  $\mu$ CT, with volumes from Prichard et al.'s (2017) study, converted from 2D measurements, for the same samples. Even assuming the maximum 2D measured diameter (average of 7.8  $\mu$ m from Prichard et al., 2017) as representative of the true diameter, Prichard et al. (2017) give an average volume of 0.25 x 10<sup>3</sup>  $\mu$ m<sup>3</sup> (Supplementary material 4.1), and their converted volumes do not surpass 420  $\mu$ m<sup>3</sup> (Fig. 4.4). Contrastingly, the average  $\mu$ CT volumes are 5 times higher, at 1.2 x 10<sup>3</sup>  $\mu$ m (Table 4.3).

# 4.8.2. The IPGE sample budget argument for PGM identification

The identification of high-density objects in each sample as laurites can be tested by applying mass balance calculations for the IPGE + Rh (Eq. 1). Since  $\mu$ CT imaging produces a 3D volume of each object, their mass can be estimated given the density. The composition of the SEM-sectioned PGE-rich phase (laurite, Table 4.5) can then be used together with the masses and compositions of other phases in the sample (chromite and silicate), to calculate the IPGE+Rh concentration of the whole sample ([IPGE + Rh]<sub>sample</sub>) because laurite is the dominant host of these elements in the sample. These calculated whole rock compositions can be compared to whole rock analyses by Barnes et al. (2016).

$$[IPGE + Rh]_{sample} = \frac{m_{laurite} \left(\overline{w}_{laurite}^{IPGE+Rh}\right)}{m_{sample}} x \ 10^9 = \frac{(V_{laurite} \ \rho_{laurite}) \ (\overline{w}_{laurite}^{IPGE+Rh})}{(V_{chromite} \ \rho_{chromite}) + (V_{silicate} \ \overline{\rho}_{silicate}) + (V_{laurite} \ \rho_{laurite})} x \ 10^9$$
(1)

In Equation 1, [IPGE + Rh]<sub>sample</sub> is the concentration of IPGE + Rh in the entire sample (ppb), V is volume (cm<sup>3</sup>, Table 4.4),  $\rho$  is density (g/cm<sup>3</sup>),  $\overline{\rho}$  is average density (g/cm<sup>3</sup>), and  $\overline{w}$  equals weight percent x 0.01 of IPGE + Rh in laurite. The ratio is multiplied by 10<sup>9</sup> to convert to ppb. We used  $\rho_{\text{laurite}}$  of 6.43 g/cm<sup>3</sup>,  $\rho_{\text{chromite}}$  of 4.5 g/cm<sup>3</sup> (Palache et al., 1944) and  $\rho_{\text{silicate}}$  of

3.3 g/cm<sup>3</sup> (average between olivine and orthopyroxene; Dana, 1892). The mass fraction of IPGE + Rh in laurites ( $\overline{w}_{laurite}^{IPGE+Rh}$ ) was taken from Prichard et al. (2017, their Table 3), by averaging Ru, Os, Ir and Rh in laurites for each layer (B, G, H, I and J). The sample, chromite, and silicate volumes are listed in Table 4.4 and the laurite volumes are listed in Table 4.3.

As discussed in section 4.6.3., this calculation ignores any laurites with volumes  $\leq 30 \,\mu\text{m}^3$ , however the mass balance calculation for IPGE + Rh (Eq. 1) is largely insensitive to the presence of these small-volume phases (a difference of 0.4 % in the total laurite volume). We compared our calculated IPGE + Rh concentrations to the measured whole rock IPGE + Rh concentrations (Table 4.6), from Barnes et al. (2016), for two cases: I) ignoring the 4 % underestimation of laurite volumes, and II) adjusting for the 4 % underestimation.

**Table 4.6.** Comparison of laurite X-ray imaging results and geochemistry.  $\Sigma = \text{sum}$ ,  $V = \text{volume in cm}^3$ ,  $\overline{w} = \text{average mass fraction}$ , \* = from Prichard et al. (2017), \*\* = from Barnes et al. (2016). The samples are composed of chromites, silicates and laurites. The adjusted laurite volume takes into account the 4 % underestimation (see text), and the [IPGE + Rh]<sub>sample</sub> – adjusted, is obtained from the adjusted laurite volume.

Sample	ST010B4	ST011G1	ST011G4	ST003H	ST014l	ST001J1
V <sub>sample</sub> (cm <sup>3</sup> )	5.8 x 10 <sup>-3</sup>	6.6 x 10 <sup>-3</sup>	7.0 x 10 <sup>-3</sup>	6.5 x 10 <sup>-3</sup>	4.8 x 10 <sup>-3</sup>	6.4 x 10 <sup>-3</sup>
$\overline{w}_{laurite}^{IPGE+Rh}$ (wt. % x 0.01) *	0.61	0.60	0.60	0.62	0.61	0.61
[IPGE+Rh] <sub>whole rock</sub> (ppb) **	354	213	239	403	243	1205
$\Sigma V_{laurite} (cm^3)$	1.8 x 10 <sup>-9</sup>	1.8 x 10 <sup>-9</sup>	1.8 x 10 <sup>-9</sup>	2.7 x 10 <sup>-9</sup>	1.0 x 10 <sup>-9</sup>	8.0 x 10 <sup>-9</sup>
$\Sigma V_{\text{laurite}} (\text{cm}^3)$ - adjusted	1.9 x 10 <sup>-9</sup>	1.9 x 10 <sup>-9</sup>	1.9 x 10 <sup>-9</sup>	2.8 x 10 <sup>-9</sup>	1.1 x 10 <sup>-9</sup>	8.3 x 10 <sup>-9</sup>
[IPGE+Rh] <sub>sample</sub> (ppb)	316	250	252	389	197	1122
[IPGE+Rh] <sub>sample</sub> (ppb) - adjusted	329	260	262	404	205	1167
[IPGE+Rh] whole rock vs. sample	89	117	105	96	81	93
(%)			Averag	e = 97 %		
[IPGE+Rh] whole rock vs. adjusted	93	122	109	100	84	97
sample (%)			Average	e = 101%		

The calculated sample IPGE + Rh values are very similar to the measured whole rock IPGE + Rh values from Barnes et al. (2016). We compare our results with Barnes et al.'s (2016) by dividing our calculated whole rock concentration of IPGE + Rh by that reported in Barnes et al. (2016) and then multiplying by 100; 100 % would indicate identical results. This comparison of our results with those of Barnes et al. (2016) demonstrate a match from 81 % to 117 %. The average match between calculated and measured values is 97 %. If we adjust the total laurite volume in a sample for the 4 % underestimation, the matches range from 84 % to 122 %, with an average match of 101 %. Our largest overestimation (22 %) might indicate a laurite missed in the whole rock analysis but present in the scanned volume and our largest underestimation (19 %) the opposite. The similarity between calculated and measured concentrations indicates that the IPGE + Rh content in all 6 samples, i.e., the total amount of IPGE + Rh reported in Barnes et al (2016), is close to the amount needed to form all identified high-density objects in a given sample, if these were laurites. In addition, based on mass balance calculations Barnes et al. (2016) determined that 10 to 16% of the IPGE are hosted by base metal sulfides. Our calculated concentrations of IPGE + Rh and the measured values agree within 20 %, strengthening our identification of high-density objects as laurites.

The above argument additionally demonstrates that few, but relatively large, laurites can account for most of the IPGE + Rh in samples many times their volume, e.g., the volume of sample ST001J1 (the sample containing the largest individual laurite),  $6.4 \times 10^{-3} \text{ cm}^3$ , is six orders of magnitude greater than the sum of all four laurite volumes ( $8.0 \times 10^{-9} \text{ cm}^3$ ) within it. Such a distribution of IPGE + Rh in a few minerals, which can be easily missed via conventional 2D methods, demonstrates both the need for accurate 3D observations and confirms that our conservative approach in determining the IPGE + Rh budget based on X-ray  $\mu$ CT was correct.

#### **4.8.3.** Origin of laurites associated with chromites in the Stillwater Complex

We examine the potential ways in which laurites formed. As previously discussed, there are currently four proposed models for laurite formation:

I) Laurites crystallize directly from the melt (Page, 1971; Prichard et al., 1981; Melcher et al., 1997);

II) Laurites crystallize at the chromite-melt interface (sourcing Ru from the melt) due to a  $fO_2$  change, and remain outside of the chromite (Finnigan et al., 2008);

III) Laurites form via exchange of IPGE (mainly Ru) from the chromite and Ni and Fe from BMS that was added to the semi-consolidated chromite cumulate (Barnes et al., 2016);

IV) Laurite and chromite are restite phases formed after hydrous melting of a sulfide-bearing pyroxenite-norite package (Mathez, 1995; Boudreau and Meurer, 1999; Boudreau, 2016; Veksler and Hou, 2020).

Our observations of the volumes and location of laurites with respect to chromites allow us to discuss aspects regarding the first three models. For the first and second models, we consider only laurites located outside of chromites and discuss the melt volume, melt availability, and time required for crystallization by sourcing the Ru in the laurite from the melt. For the third model, we consider only laurites found within chromites, and discuss Ru availability and Ru diffusion within single and multiple chromites. In all cases, we assume laurites have formed at the location where they were imaged. Our results do not provide evidence for, or against, the fourth model and it will not be discussed further in this contribution.

#### **4.8.3.1.** Laurite crystallization from a silicate melt

The first and second model consider a silicate melt as the IPGE source for laurite crystallization (here we will focus on Ru). In the first model, laurite crystallization is not tied to another phase, while in the second; chromite and laurite crystallize at the same time. Crystallization of laurite was experimentally shown to occur very close to the chromite, in the chromite-melt boundary region (CMBR), defined by Finnigan et al. (2008) as: "the region between the melt-crystal interface and the outermost extent of the region in which diffusion occurs as a result of chromite growth". In this region of chromite growth there is a local decrease in  $fO_2$ , leading to a drop of Ru and Os solubility by up to 22 %, resulting in laurite nucleation (Finnigan et al., 2008). The third model proposes chromites as efficient PGE-collectors in PGM-unsaturated magmas, such as the Bushveld B1 magma (Harmer and Sharpe, 1985; Barnes and Maier, 2002). The Bushveld B1 magma was chosen due to its PGE-compositional similarity to primary mantle magmas (Barnes et al., 2010).

From the perspective of a melt (the Ru-source), the location of a laurite in relation to a chromite is irrelevant. If a laurite is pinned to a chromite, access to the melt is more restricted as it is not surrounded by the melt on all sides and as its movement through the melt is governed by the chromite (the larger phase). Here we will examine melt availability for this restrictive scenario.

The chromites sink through the magma column as they grow, and it is unknown how much laurite growth occurred during or after chromite sinking and settling. During chromite sinking, settling and compaction, laurites must scavenge Ru from the surrounding melt to grow and they must access enough Ru to achieve the volumes found in our samples. The initial laurite crystal nuclei would have to interact with a potentially large volume of melt to reach their final volumes of  $0.05 \times 10^3$  to  $7.54 \times 10^3 \mu m^3$  (Table 4.3).

According to the latest Stillwater emplacement ages (Wall et al., 2010; Wall et al., 2018), the Peridotite Zone (Fig. 4.1) cooled from 1300 °C to 850 °C (zircon closure) from 2711.4 Ma to 2710.4 Ma, i.e., some magma was present for at most 1 Ma. Since Ru is a major element in laurite, we assume that laurite crystallization, at a fixed  $fO_2$ , is controlled by RuS<sub>2</sub> saturation in the chromite-melt boundary region and that all the Ru would partition into the laurite (an overestimation), therefore calculating the minimum amount of melt needed.

### The required melt volume for laurite crystallization

Modifying the equation used in Barnes et al. (2016), the amount of melt the laurite would need to obtain sufficient Ru to grow to a specified volume can be calculated as follows (Eq. 2-4):

$$m_{melt} [Ru]_{melt} = m_{laurite} [Ru]_{laurite}$$
(2)

$$V_{melt} \ \rho_{melt} \ [Ru]_{melt} = V_{laurite} \ \rho_{laurite} \ [Ru]_{laurite}$$
(3)

$$V_{melt} = \frac{V_{laurite} \ \rho_{laurite} \ [Ru]_{laurite}}{\rho_{melt} \ [Ru]_{melt}} \tag{4}$$

In Equations 2-4  $m_{melt}$  is the mass of the melt (g),  $m_{laurite}$  is the mass of the laurite (g),  $V_{melt}$  is the volume of the melt (cm<sup>3</sup>), [Ru]<sub>laurite</sub> is the Ru concentration in the laurite (48.34 wt. % x 0.01),  $\rho_{laurite}$  is the laurite density (6.43 g/cm<sup>3</sup>),  $V_{laurite}$  is the laurite volume (cm<sup>3</sup>) and  $\rho_{melt}$  is the melt density (2.68 g/cm<sup>3</sup>, the peridotite melt density from Lesher and Spera, 2015). [Ru]<sub>melt</sub> is the concentration of Ru in the melt (1.9 x 10<sup>-7</sup> wt. % x 0.01, or 1.9 ppb, from the B1 melt of the Bushveld Complex, Harmer and Sharpe, 1985; Barnes and Maier, 2002). The Ru concentration in the laurite (48.34 wt. %) is the average value of Ru in laurites from layers B, G, H, I and J, taken from Prichard et al. (2017, their Table 3). The calculations are simplified by assuming all Ru from the melt will partition into the laurite. The calculation results are shown in Table 4.7.

**Table 4.7.** Volumes of measured interstitial laurites and the calculated melt volumes needed to form them. V = volume in  $\mu$ m<sup>3</sup> or m<sup>3</sup>,  $\Sigma$  = sum. The calculated melt volumes per laurite are summed for the two laurites in sample ST003H.

Sample	ST0011G1	ST011G4	ST003H		ST001J1
V <sup>measured</sup> (µm <sup>3</sup> )	1843	1846	59	189	7540
V <sup>calculated</sup> (m <sup>3</sup> )	1.12 x 10 <sup>-6</sup>	1.12 x 10 <sup>-6</sup>	$0.03 \times 10^{-6}$ $\Sigma = 0.15$	0.11 x 10 <sup>-6</sup> 5 x 10 <sup>-6</sup>	4.58 x 10 <sup>-6</sup>

Since here the melt is the sole source of Ru, the melt volume is positively correlated to the laurite volume ( $R^2 = 1$ ). Laurites would need to interact with at least 0.03 x 10<sup>-6</sup> m<sup>3</sup> (for a laurite of 59 µm<sup>3</sup> in sample ST003H) and up to 4.58 x 10<sup>-6</sup> m<sup>3</sup> (for a laurite 7540 µm<sup>3</sup> in sample ST001J1) of melt to reach their measured volumes. The average amount of melt, across all four samples, would be 1.39 x 10<sup>-6</sup> m<sup>3</sup> per laurite. As the melt and laurite volumes are related through Equation 4, we always need 6.08 x 10<sup>8</sup> more melt than laurite.

# Chromitite layer formation time and melt availability

We next examine the availability of the required melt volume. The lowest estimate of the melt volume that passed through the entire Ultramafic Series (Peridotite Zone + Upper Bronzitite Zone, Fig. 4.1) is 70 x  $10^3$  km<sup>3</sup> (Lipin and Zientek, 2002), representing the minimal amount of melt available to phases crystallizing directly from the melt. If we assume that all Ru in the melt becomes incorporated into laurites, and that laurites grew solely from the melt, we see that the average  $1.39 \times 10^{-6}$  m<sup>3</sup> of melt needed for laurite formation would be easily accommodated. However, chromite settling and chromite layer formation are melt volume restricting events, as they produce an environment where crystals are packed (closely) together 172

and no longer surrounded by melt on all sides. Consequently, the space through which melt can be displaced becomes restricted to spaces between compacted chromite crystals (a "Sinetwork" of pathways). The volume of melt accessible to each crystal becomes thus restricted as well.

We can calculate the duration of both chromite settling and layer formation. We examine a simplified case where: I) chromites grow during sinking, settling, and layer compaction, but at a minimal rate solely to allow for laurite formation and growth, II) laurite crystal nuclei are formed in the chromite-melt boundary region immediately prior to chromite sinking and remain attached to the chromite, and III) layer compaction is solely mechanical (not chemical, i.e., we disregard chromite dissolution-precipitation). A schematic of these processes is presented in Figure 4.9.

The velocity of sinking chromites is obtained through Stokes law (Eq. 5, Stokes, 1851):

$$v_s = \frac{d^2 \,\Delta\rho \,g}{18\,\mu} \qquad (5)$$

In Equation 5: v<sub>s</sub> is the sinking velocity in m/s, d is the chromite diameter in m,  $\Delta \rho$  is the chromite-melt density difference in kg/m<sup>3</sup>, g is the gravity acceleration in m/s<sup>2</sup> and  $\mu$  is viscosity in Pa s. The chromite diameter is obtained from the average chromite volume  $(\bar{V}_{chromite}^{grain}$  in Table 4.4) through  $\bar{d}_{chromite}^{grain} = 2 * \sqrt[3]{\frac{3\bar{V}_{chromite}^{grain}}{4\pi}}$ . The density difference is calculated as  $\rho_{chromite} - \rho_{Si-melt} = 4500 \text{ kg/m}^3 - 2689 \text{ kg/m}^3 = 1811 \text{ kg/m}^3$ . We used a viscosity value of 25.7 Pa s (Giordano et al., 2008). The sinking velocities ( $v_{sinking}^{chromite grain}$ ) are reported in Table 4.8.

To obtain a maximum sinking time ( $t_{sinking}^{chromite}$ , Table 4.8), we simplify and assume all chromites that form a layer at the bottom of the unsolidified sill, crystallized at its top (Fig. 4.9A), and divide the sinking path with the sinking velocity. The Stillwater layered intrusion

was emplaced at 12-16 km depth (Thomson, 2008; Hanley et al., 2008) and its current uneroded remaining thickness is 5.3 km (Todd et al., 1982). Estimates of original chamber height range between ~ 6 km to almost to the surface, 12 to 16 km (Lipin and Zientek, 2002). For the purpose of this simplistic scenario, we will assume a 12 km emplacement depth of an intruding sill, 2 km unsolidified sill height and 10 km of overlying rocks. The 2 km sill thickness is obtained by ignoring subdivisions within the Peridotite Zone to individual chromitite layers (which can be found in Cooper, 2002) and instead considering only the thickness between layers G1 and H1, which is approximately 100 m. Considering 5% fractional crystallization of the silicate melt (Lipin, 1993), we would need a maximum of 2 km of melt. As we are interested in obtaining the longest possible times (to see if all events can occur within 1 Ma), henceforth we will present a simplistic scenario with a 2 km sinking path. If we take the entire sill thickness (which we will here consider as height) as the 2 km melt column, we obtain sinking times from ~ 30 years for layer J and ~ 45 years for layer G (Table 4.8).

Close to the unsolidified sill bottom, many chromites are settling simultaneously, and they settle as a suspension of melt + chromite + laurite, so we calculate their hindered settling velocity (Eq. 6) given in Manoochehri and Schmidt (2014, and references therein) as:

$$v_{\varphi_C} = v_s (1 - \varphi_C)^n \qquad (6)$$

In Equation 6  $v_{\phi c}$  is the hindered settling velocity in m/s,  $v_s$  is the Stokes settling velocity in m/s,  $\phi_c$  is the chromite fraction in the suspension and *n* is the sedimentation exponent. We have obtained  $v_s$  from Equation 5 and applied a sedimentation exponent of 2.35 (Manoochehri and Schmidt, 2014). For the chromite fraction in the suspension we used 0.012 which corresponds to 1.2 vol. % chromite in the parental magma (Mondal and Mathez, 2008), a value considered as the maximum possible amount. The fraction of silicate melt in the suspension would thus be 98.8 vol. %, while the fraction of laurite would be unappreciable.

Solutions for Equations 5 and 6 allow us to solve for the chromitite layer settling time (Eq. 7, Table 4.8; Manoochehri and Schmidt, 2014):

$$t_{settling}^{layer} = \frac{\frac{0.48 \ h}{\varphi_{Ci}} - h}{v_{\varphi_{C}}}$$
(7)

In Equation 7:  $t_{settling}^{layer}$  is the time needed for all chromites that comprise a layer to settle (stop sinking) in s, *h* is the resulting layer thickness in m,  $v_{\varphi c}$  is the hindered settling velocity in m/s (obtained from Eq. 6) and  $\varphi_{Cl}$  is the chromite fraction in the initial melt layer from which the final layer forms. It is important to note that while Manoochehri and Schmidt (2014) differ between  $\varphi_C$  and  $\varphi_{Cl}$  for their centrifuge chromite settling and compaction experiments, in a natural case they are the same, 0.012. For the thickness of the considered layers, we took values from Cooper (2002). We simplified the model by treating the entire layer as composed only of chromite, while actually a layer consists of chromities separated by chromite-bearing pyroxenite or peridotite (Cooper 2002). The final chromite fraction in the gravitationally formed, non-compacted layer is 0.48, and 0.52 is the layer's average fraction of silicate melt in the experiments of Manoochehri and Schmidt (2014). Settling is complete once the silicate melt fraction decreases to 0.52 (Manoochehri and Schmidt, 2014). Following Manoochehri and Schmidt (2014) we refer to this melt fraction as the porosity in the subsequent discussion.

Compaction follows settling, and Manoochehri and Schmidt (2014) define compaction time as the time needed to reduce layer porosity from 0.52 to the final measured porosity (their, and our, Eq. 8):

$$t_{compaction}^{layer} = \frac{5.471 \, x \, 10^{18}}{10^{(14.35 \, \varphi)}} \, x \, \frac{d}{h \, \Delta \rho} \quad (8)$$

In Equation 8  $t_{compaction}^{layer}$  is the time in s needed for the layer porosity ( $\varphi$ ) to decrease from 0.52 to its final value (volume ratio of silicates found in Table 4.4), d is the mineral diameter

in m, h is the depth within a cumulate pile, here taken as the layer thickness, and  $\Delta \rho$  is the chromite-melt density difference of 1811 kg/m<sup>3</sup>.

Stillwater chromitite samples display variable parameters, with layer thicknesses varying from ~ 0.02 m (layer J1) to ~ 0.4 m (layer G1), final porosities (silicate fraction) from 0.11 to 0.36, and average chromite diameters from  $1.60 \times 10^{-4}$  to  $2.47 \times 10^{-4}$  m. Consequently, the calculated compaction times are highly variable across all chromite layers, from ~ 0.4 years (~ 140 days) for layer G1 to 30 k years for layer J1 (Table 4.8).

The total layer formation time,  $t_{formation}^{layer}$  is (Eq. 9):

$$t_{formation}^{layer} = t_{sinking}^{chromite} + t_{settling}^{layer} + t_{compaction}^{layer}$$
(9)

The layer formation times (Table 4.8) are variable, ranging from ~ 65 years for layer G4 and ~ 30 k years for layer J1, due to different grain size, layer thickness and final porosity, but all are shorter than 1 Ma. If we have overestimated the unsolidified sill thickness (and thus the sinking path) or underestimated the chromite crystal volume (for layer G4), the layer formation time would be even shorter.



**Figure 4.9.** A schematic representation of laurite formation within the chromite-melt boundary region. Image not to scale. A) Chromites (in dark grey) crystallize from a silicate melt within an unsolidified magmatic sill and start to sink. The 20 µm wide area adjacent to the chromite-melt interface is the chromite-melt boundary region (CMBR, in light grey; Finnigan et al., 2008), where laurites crystallize (in yellow). B) At the bottom of the sill, the sunken chromites have settled and compacted into a layer through which melt is percolating (motion depicted with arrows). C) Enlarged view of panel B. The chromite-melt boundary region does not encompass the entire width of melt pathways between compacted chromites.

**Table 4.8.** Chromitite layer formation and characterization.  $\overline{d}$ = average mineral grain diameter in m, v = velocity in m s<sup>-1</sup>, t = time in years,  $\overline{h}$  = average layer thickness in m,  $\varphi$  = porosity (dimensionless), Si-network = silicate phases in a sample.

Sample	ST0011G1	ST011G4	ST003H	ST001J1
	1			
$d_{grain}^{chromate}$ (m)	2.47 x 10 <sup>-4</sup>	1.60 x 10 <sup>-4</sup>	2.08 x 10 <sup>-4</sup>	2.26 x 10 <sup>-4</sup>
v <sup>chromite grain</sup> (m s <sup>-1</sup> )	2.33 x 10 <sup>-6</sup>	9.78 x 10 <sup>-7</sup>	1.66 x 10 <sup>-6</sup>	1.96 x 10 <sup>-6</sup>
t <sup>chromite</sup> (y)	27.15 64.80		38.18	32.34
	Layer avera	.ge = 45.98		
$\overline{h}_{layer}(\mathbf{m})$	0.4	0.3	0.06	0.02
t <sup>layer</sup> settling (y)	0.21	0.39	0.04	0.01
	Layer average = 0.30			
$\varphi \left( V_{Si-network} / V_{sample} \right)$	0.11	0.36	0.21	0.11
	Layer avera	age = 0.23		
$m{t}_{compaction}^{layer}\left(\mathbf{y} ight)$	1403.07	0.39	290	30000
	Layer averag	ge = 701.73		
t <sup>layer</sup> (y)	1430.44	65.58	328.99	30032
	Layer averag	ge = 748.01		
$V_{melt}^{calculated}/V_{Si-network}$	1500.99	450.13	109.09	6604.99

#### *Melt percolation through the chromitite layer*

In previous section we modeled the required amount of melt for laurites found outside of chromites to grow to their measured volumes, assuming all Ru present in the melt becomes incorporated into laurites. We have also shown that chromitite layers can form in a few 100 years (Table 4.8.). We next consider how long the required melt volume needs to percolate through the chromitite layer ( $t_{percolation}^{melt}$ ) if there was no laurite growth during chromitite layer formation (Fig. 4.9B). We do not consider chromite crystallization rates nor reactive melt percolation, but simplistically examine could there have been enough melt for interstitial laurites to form and grow to the sizes we observed.

In a layer of closely packed chromites, the volume through which the melt can percolate will later become solidified as silicate phases (Fig. 4.7B), i.e., a "Si-network" that represents melt pathways. If we compare the melt needed for laurite crystallization with the Si-network volume (Table 4.4), there would need to have been from ~ 100x (layer H) to ~ 6300x (layer J) more melt circulating through the Si-network than the network could have accommodated at any given time (Table 4.8).

To obtain the melt percolation time, we need to calculate layer permeability and the flow rate. We calculate the permeability (k) by applying the Carman-Kozeny equation (Carman, 1937; Eq. 10):

$$k = \frac{\frac{\varphi^3 x \, d^2}{c}}{(1-\varphi)^2} \qquad (10)$$

In Equation 10 *k* is the permeability in  $m^2/s$ ,  $\varphi$  is the final porosity (Table 4.9), *d* is the mineral grain diameter in m, and *C* is a parameter that depends on microscopic hydraulic bond geometry, and equals 10 (Connolly et al., 2009).

We then calculate the flow rate (Q) by applying Darcy's law (Darcy, 1856; Eq. 11):

$$Q = \frac{k \ A \ \Delta P}{h \ \mu} = \frac{k \ A \ (\rho_{melt} \ h_{column}^{melt} + \rho_{crust} \ h_{thickness}^{overlying \ rocks}) \ g}{h_{thickness}^{chromite \ layer} \ \mu} \tag{11}$$

In Equation 11 Q is the flow rate in m<sup>3</sup>/s, k is the permeability in m<sup>2</sup>/s, A is the cross-section area of a scanned sample in m<sup>2</sup>,  $h_{thickness}^{chromite layer}$  is the layer thickness in m,  $\mu$  is viscosity in Pa s (25.7 Pa s). The pressure difference  $\Delta P$  is defined as  $\rho x g x h$ , and is the sum of the pressure of the melt column above the chromitite layer and the lithostatic pressure of the overlying rocks, where g is 9.81 m/s<sup>2</sup>,  $\rho_{melt}$  is 2689 kg/m<sup>3</sup>,  $h_{column \ height}^{melt}$  is 2000 m,  $\rho_{crust}$  is 2800 kg/m<sup>3</sup> (average crustal density from Dziewonski and Anderson, 1981) and  $h_{thickness}^{overlying \ rocks}$  is 10000 m.

To obtain the melt percolation time  $(t_{percolation}^{melt})$ , we divide the needed melt volume  $(V_{melt}^{calculated})$  with the flow rate (Eq. 12):

$$t_{percolation}^{melt} = \frac{V_{melt}^{calculated}}{Q} \quad (12)$$

We performed the calculation for three scenarios (Table 2.9): I) using the maximum sample (i.e., entire layer) porosity, II) using only the volume of the 20  $\mu$ m edges of the Sinetwork, and III) using previously published interstitial melt flow rates (Sparks et al., 1985, Tegner et al., 2009, Yao et al., 2019).

Considering the entire sample porosity, we assume a laurite can scavenge the entire melt volume occupying the Si-network. The percolation times range from 0.07 hours (~ 4 min) for layers H and G4 to 3.47 hours for layer J1.

However, the melt in the Si-network might not be accessible in its entirety to the laurite nucleus. Finnigan et al.'s (2008) chromite –melt boundary region extends at most 20 µm from the chromite-melt interface (based on their Fig. 4.5A). Thus, only the 20-µm edges of the Si-network constitute the available melt (Fig. 4.9C). After extracting the 20-µm Si-network edge volume (by eroding the Si-network volume for 20 µm and subtracting this smaller volume from 181

the original volume), we calculate the effective porosity,  $\varphi_{effective}$ , as  $V_{Si-network \ 20-\mu m \ edges}/V_{sample}$  (Table 4.9). Using the effective porosity, the permeability is lower, flow rate is slower and melt percolation time is longer. The new percolation time ranges from 0.17 hours (~ 10 min) for layer H to ~ 8 h for layer J1.

The third scenario entails a different approach where we apply an interstitial melt flow rate ( $Q_{interstitial}$ ) of ~ 1 m/y (Sparks et al., 1985, Tegner et al., 2009, Yao et al., 2019), which is between 135x and 670x faster than our calculated 20-µm edge flow rates (for samples H and G1, respectively). In this case, melt percolation times range from ~ 5 sec for layer H and ~ 2 min for layer J1 (Table 4.9). In all three scenarios, the percolation times are geologically instantaneous.

Our layer formation times and melt percolation times yield the same conclusion; there was sufficient melt volume available for interstitial laurites to grow to their measured volumes in an extremely short time. In fact, the times are so short, that we question why are the interstitial laurites so small?

Based on their experimental findings, Finnigan et al. (2008) suggested chromites have the capability of scavenging the silicate melt for IPGE, yet the laurites within the chromitemelt boundary region are few and smaller than expected. A potential reason might be their incorporation into chromites. Initially, we disregarded chromite growth, but chromites grow during sinking, settling, compaction and melt percolation until layer solidification. Their subsolidus growth is inferred through chromite morphology (triple junctions, Barnes et al., 2016) and crystal size distribution (Waters and Boudreau, 1996). We have considered only interstitial laurites and X-ray  $\mu$ CT does not offer information to evaluate the number of laurites that potentially nucleated within the chromite-melt boundary region, but subsequently became enclosed within chromites. However, we have not identified many minute laurite inclusions, parallel to the chromite-melt interface, as Finnigan et al. (2008) suggest, but only a few large and dispersed laurites. There might be laurites below the spatial resolution of our  $\mu$ CT study, but no 2D study reports such small inclusions (e.g., Prichard et al., 2017).

Another reason for the lack of small laurites, either in the chromite-melt boundary region or as inclusion strings, could still be melt unavailability, as some laurites are located between densely packed chromites (e.g., in chromite triple junctions, Fig. 4.5B), where melt percolation is further restricted or perhaps even stagnant. Examining melt availability at such occluded locations would require melt flow modelling that is beyond the scope of this work.

Based on our 3D observations of laurite volumes and melt and time calculations, we suggest that although chromite-melt boundary conditions may lead to PGM formation, they cannot efficiently sustain PGM growth. The identified development of a  $fO_2$  change in the chromite-melt boundary region recognized in Finnigan et al.'s (2008) work shows that PGM formation is possible there. They have not imposed any constraints on the maximum volume a PGM could reach through this mechanism. It is clear that in order for a mineral to grow, a supply of melt needs to be maintained, provided the melt is the sole source of elements. Our modelling has shown that there were no impediments in melt supply, prompting us to question the small interstitial laurite volumes.

**Table 4.9.** Melt percolation times for different permeabilities and flow rates. Si-network = silicate phases in a sample,  $\varphi$  = porosity (dimensionless), k = permeability in m<sup>2</sup>, Q = flow rate in m<sup>3</sup> s<sup>-1</sup>, t = time in hours.

Sample	ST0011G1 ST011G4		ST003H	ST001J1
Maximum porosity				
$\varphi(V_{Si-network}/V_{sample})$	0.11 0.36 Layer average = 0.23		0.21	0.11
k (m <sup>2</sup> )	1.12 x 10 <sup>-11</sup>	2.78 x 10 <sup>-10</sup>	6.75 x 10 <sup>-11</sup>	8.20 x 10 <sup>-12</sup>
Q (m <sup>3</sup> s <sup>-1</sup> )	1.60 x 10 <sup>-10</sup>	3.99 x 10 <sup>-9</sup>	5.80 x 10 <sup>-10</sup>	3.52 x 10 <sup>-10</sup>
tcalculated melt tlayer percolation (h)	1.86         0.07           Layer average = 0.97		0.07	3.47
Effective porosity				
V <sub>Si-network</sub> 20-µm edge (µm <sup>3</sup> )	5.11 x 10 <sup>8</sup>	1.10 x 10 <sup>7</sup>	1.07 x 10 <sup>7</sup>	5.33 x 10 <sup>8</sup>
Peffective	0.08	0.16	0.16	0.08
$(V_{Si-network \ edge}/V_{sample})$	Averag	e = 0.12		
k (m <sup>2</sup> )	3.30 x 10 <sup>-12</sup>	1.41 x 10 <sup>-11</sup>	2.73 x 10 <sup>-11</sup>	3.51 x 10 <sup>-12</sup>
$Q (m^3 s^{-1})$	4.73 x 10 <sup>-11</sup>	2.02 x 10 <sup>-10</sup>	2.34 x 10 <sup>-10</sup>	1.51 x 10 <sup>-10</sup>
t calculated melt t layer percolation (h)	6.31 Layer aver	1.48 rage = 3.89	0.17	8.10

Literature flow rates (Sparks et al., 1985, Tegner et al., 2009, Yao et al., 2019) = $1 \text{ m}^3 \text{ y}^{-1}$							
Q <sub>interstitial</sub> (m <sup>3</sup> s <sup>-1</sup> )	3.17 x 10 <sup>-8</sup>						
t <sup>calculated melt</sup> (h)	9.43 x 10 <sup>-3</sup> Average =	9.45 x 10 <sup>-3</sup> 9.44 x 10 <sup>-3</sup>	1.27 x 10 <sup>-3</sup>	3.86 x 10 <sup>-2</sup>			
t <sup>calculated melt</sup> t <sub>layer percolation</sub> (s)	33.95 Layer aver	34.01 age = 33.98	4.57	138.92			

#### Sulfide melt presence and contribution to laurite formation

The laurite formation model of Barnes et al. (2016) proposes that a BMS liquid was added to the unconsolidated chromite cumulate pile and percolating through it. The BMS originating from this liquid would then be mostly converted to laurite through diffusive element exchange (Barnes et al., 2016). We have not found BMS using X-ray  $\mu$ CT, perhaps due to our small sample number, but their presence in these samples has been unequivocally documented (e.g., Barnes et al., 2016; Wavrant, 2017). Barnes et al. (2016) found very small BMS (< 1 micron) in almost 40 % of chromite inclusions, and Wavrant (2017) found interstitial BMS with an average size of 25  $\mu$ m.

Barnes et al. (2016) already considered sulfide liquid settling and downward sulfide droplet infiltration into the semi-consolidated chromite cumulate pile (Chung and Mungall, 2009), but it is difficult to constrain the total sulfide liquid volume needed to apply percolation calculations. In addition, it is still not possible to constrain the chromite-sulfide diffusive exchange, as the diffusion coefficients have not been determined.

Our 3D observations show a variable Si-network morphology, with porosities up to 0.36, able to accommodate the percolation of 0.01 - 0.1 mm sized sulfide droplets (Barnes et al., 2016), but also with areas of densely packed chromites, able to trap them. Unobstructed sulfide liquid percolation is achieved at very small fractions. Sulfide melt wets chromites extremely efficiently (Brenan and Rose, 2002), with an equilibrium dihedral angle  $\theta = 11^{\circ}$  (Koegelenberg, 2012), far below the cut-off angle of 60° (Blander and Katz, 1975; Barnes et al., 2017) and can thus form interconnected 3D channels at small melt fractions (von Bargen and Waff, 1986; Wark et al., 2003). Additionally, the presence of silicate melt is important in ensuring adequate sulfide liquid mobility (Mungall and Su, 2005), so that the latter does not become retained within the chromite cumulate pile (Koegelenberg, 2012). Silicate melt and sulfide liquid engage in competitive wetting along non-silicate mineral surfaces and borders,
so their mutual displacement furthers their percolation (Barnes et al., 2017). Our high porosities (0.11 - 0.36) could have lowered the potential for sulfide melt retention, either prior to postcumulus chromite growth or during chromite growth and sintering.

#### **4.8.3.2.** Laurite formation by diffusion within chromites

To investigate whether laurites could have grown to our measured 3D volumes solely through diffusion of Ru within a chromite we consider several scenarios involving different laurite and chromite volumes. We focus on the nine laurites found completely within chromites, in samples ST010B4, ST003H, ST014I and ST001J1. Modifying Equation 4 for the case of laurite growing only from Ru in its host chromite ( $V_{chromite}^{measured}$ ), we obtain the following mass balance expression (Eq. 13) for the calculated volume of laurite ( $V_{laurite}^{calculated}$ ):

$$V_{laurite}^{calculated} = \frac{V_{chromite}^{measured} \rho_{chromite} [Ru]_{chromite}}{\rho_{laurite} [Ru]_{laurite}}$$
(13)

In Equation 13 V is the volume (cm<sup>3</sup>),  $\rho$  is the density (g/cm<sup>3</sup>) and [Ru] is the concentration of Ru (wt. % x 0.01). We used  $\rho_{\text{laurite}}$  of 6.43 g/cm<sup>3</sup> and  $\rho_{\text{chromite}}$  of 4.5 g/cm<sup>3</sup> (Palache et al., 1944). For the Ru concentration in chromite, we used the value of 4.14 x 10<sup>-5</sup> wt. %, or 0.414 ppm, for ([*Ru*]<sup>*natural*</sup><sub>*chromite*</sub>) that represents measured Ru in natural chromites from Pagé and Barnes (2016). The Ru concentration in laurite is 48.34 wt.% (Prichard et al., 2017). The difference between the measured and the calculated laurite volumes is schematically presented in Figure 4.10A.

For each measured chromite volume, we compare the measured laurite volume against our calculated laurite volume (Table 4.10). If the laurite nucleated and grew solely from Ru originally in the enclosing chromite, then the larger the chromite the larger the laurite. However, there is no correlation ( $R^2 = 0.03$ ) between the measured volumes of chromites and laurites. The measured laurite volumes are larger than the calculated ones, from ~ 2x (second laurite in sample ST014I) to  $\sim$  150x (sample ST010B4), for all cases but one – for the first laurite in sample ST001J1, the measured laurite is 0.65x smaller than the calculated one. This shows that in almost all cases single chromites that host the laurites did not contain sufficient Ru for the measured laurite volumes.

**Table 4.10.** (following page) Results of mass balance calculations shown in Equations 13-18 (see text). Comparison of measured and calculated laurite volumes for each chromite containing a laurite. Hypothetical calculated Ru concentration and chromite volumes are also presented. V = volume in in  $\mu$ m<sup>3</sup>, [Ru] = Ru concentration in ppm, r = radius in in  $\mu$ m.

Sample	ST010B4		ST003H		ST	014I	S	T001J1	
measured 3	$2.07 - 10^7$	1.40	5.75 x	1.59	2.79	9.48 x	5.44 x	5.20	1.37
ν <sub>chromite</sub> (μm)	2.07 x 10'	x 10 <sup>8</sup>	10 <sup>7</sup>	x 10 <sup>8</sup>	x 10 <sup>7</sup>	107	10 <sup>8</sup>	x 10 <sup>7</sup>	x 10 <sup>7</sup>
r <sup>equivalent sphere</sup> r <sub>chromite</sub> (μm)	171	322	239	337	188	283	506	232	149
calculated ( )	10.14	83.9	<b>2</b> 4 40	95.9	16.7		326.13	31.1	8.25
Vlaurite (µm <sup>3</sup> )	12.46	7	34.49	4	6	56.89		9	
V <sup>measured</sup> (μm <sup>3</sup> )	1840	1963	269	249	683	353	213	126	135
[Ru] <sup>calculated</sup> (ppm)	61.17	9.67	3.24	1.07	18.5 3	0.72	0.27	1.66	6.79
in acalculated		23.3			44.7				16.3
$[Ru]_{chromite}^{(Ru]_{natural}}$	147.65	4	7.82	2.58	3	1.74	0.65	4.00	9
hypothetical		3.27	4.5 x	4.17	1.14	5.88 x	3.54 x	2.09	2.26
$V_{chromite}^{hypotheticul}$ (µm <sup>3</sup> )	3.07 x 10 <sup>9</sup>	x 10 <sup>9</sup>	10 <sup>8</sup>	x 10 <sup>8</sup>	x 10 <sup>9</sup>	10 <sup>8</sup>	10 <sup>8</sup>	x 10 <sup>8</sup>	x 10 <sup>8</sup>
	0.01.05	920.		463.	647.		100.00	368.	377.
r <sub>scavenging</sub> (μm)	901.37	56	475.43	39	65	519.69	439.02	40	62
$\overline{V}_{chromite}^{individual}$ (µm <sup>3</sup> )	2.06 x 10 <sup>6</sup>		4.71 x 10 <sup>6</sup>	5	4.35	x 10 <sup>6</sup>	6.	04 x 10 <sup>6</sup>	5
r <sup>equivalent sphere</sup> chromite (μm)	78.93		103.98		10	1.26		112.98	
$N_{scavenged}$ chromites	1489	694	96	88	262	135	1	35	37



**Figure 4.10**. A schematic representation of different chromite and laurite volumes measured in 3D or obtained through mass balance calculations. The relationships represent all cases but the first laurite-chromite pair in sample ST001J1. A) A real (measured) chromite, shown in light grey, whose volume we measured in 3D, contains a real, also measured, laurite volume, shown in yellow. The calculated laurite volume, shown in orange, is the maximum that should form solely from Ru within that single chromite. Measured laurite volumes are always larger than calculated ones. B) To form the laurite included in the chromite, the chromite volume should be many times larger than it is and is presented here as the hypothetical chromite volume, shown in dark grey. C) To grow to its measured volume, the laurite must scavenge chromites that fall under the hypothetical calculated chromite volume for Ru. The distance the Ru must diffuse to form the laurite is the scavenging radius.

By modifying Equation 4 we can calculate the necessary Ru concentration that each measured host chromite should contain  $([Ru]^{calculated}_{chromite})$ , to be the sole Ru supplier for the measured laurite volumes (Eq. 14):

$$[Ru]^{calculated}_{chromite} = \frac{\frac{V^{measured}_{laurite}}{\rho_{laurite}} \rho_{laurite}}{\frac{\rho_{laurite}}{\rho_{chromite}}} \qquad (14)$$

For the purpose of Table 4.10 and for a more direct comparison with natural chromite values, the Ru concentration is reported in ppm. As expected, the [Ru]<sup>calculated</sup><sub>chromite</sub> values in Table 4.10 are higher than 0.414 ppm, from  $\sim 2x$  (third laurite in sample ST003H and second laurite in sample ST014I) to ~ 150x for sample ST010B4. The reverse holds for the first lauritechromite pair in sample ST001J1, as the pair consists of a very large chromite (90x larger than the average chromite volume for that sample; Tables 4.4, 4.10) containing a relatively small laurite (when compared to other measured laurites, Table 4.10).

Since a single chromite holds insufficient Ru, we next consider the volume of chromite needed to scavenge Ru, supposing a single laurite could scavenge multiple chromites. We can approximate the scavenging distance by calculating the volume of a hypothetical chromite  $(V_{chromite}^{hypothetical}$  in Table 4.10, Eq. 15, Fig. 4.10B) whose radius  $(r_{scavenging}$  in Table 4.10, Eq. 16, Fig. 4.10C) is large enough to supply the necessary Ru for the observed laurites, assuming  $V_{chromite}^{hypothetical}$  is a sphere:

$$V_{chromite}^{hypothetical} = \frac{V_{laurite}^{measured} \rho_{laurite} ([Ru]_{laurite} x \, 10^{-2})}{\rho_{chromite} [Ru]_{chromite}^{natural}}$$
(15)  
$$r_{scavenging} = \sqrt[3]{\frac{4 \ V_{chromite}^{hypothetical}}{3 \pi}}$$
(16)

 $V_{chromite}^{hypothetical}$  is always larger than  $V_{chromite}^{measured}$ , except for the first laurite-chromite pair in ST001J1. If we compare the  $V_{chromite}^{hypothetical}$  from Table 4.10 to the volume of all chromites in a sample (  $V_{chromite}^{total}$  from Table 4.4), for the nine samples that contain chromite-hosted laurites,  $V_{chromite}^{hypothetical}$  is always smaller, but not greatly so: 3.07 x 10<sup>9</sup>  $\mu$ m<sup>3</sup> vs. 3.14 x 10<sup>9</sup>  $\mu$ m<sup>3</sup> for sample

3π

ST010B4, 4.1 x  $10^9 \,\mu\text{m}^3$  (sum of 3 volumes) vs. 5.16 x  $10^9 \,\mu\text{m}^3$  for sample ST003H, 1.4 x  $10^9 \,\mu\text{m}^3$  (sum of 2 volumes) vs. 3.62 x  $10^9 \,\mu\text{m}^3$  for sample ST014I and 7.89 x  $10^8 \,\mu\text{m}^3$  (sum of 3 volumes) vs. 5.72 x  $10^9 \,\mu\text{m}^3$  for sample ST001J1. Thus, the scanned sample volume holds sufficient Ru to account for all the chromite-hosted laurites within it.

The scanned samples contain numerous chromites, and we can approximate the number of chromites the laurites need to scavenge Ru from ( $N_{scavenged chromites}$ ) by dividing  $V_{chromite}^{hypothetical}$  by the average individual chromite volume for each sample ( $\overline{V}_{chromite}^{individual}$ , Tables 4.4 and 4.10). The number of chromites needed ranges from 38 in sample ST014I to 1489 in sample ST010B4 and is positively related to laurite volume ( $\mathbb{R}^2 = 0.99$ ) if sample ST010B4 is omitted. The latter contains a large laurite among chromites that are smaller than in other samples. If sample ST010B4 is included, the correlation drops to  $\mathbb{R}^2 = 0.79$ . For the first lauritechromite pair in sample ST001J1, the calculation yields 59 chromites to scavenge, when in reality only one, the host chromite, is sufficient. For the same reason, the pair's  $r_{scavenging}$  is smaller than the chromite's  $r_{chromite}^{equivalent sphere}$  (~ 440 µm and ~ 500 µm, respectively). If two laurites were closer than the sum of their respective scavenging distances they would be competing for Ru, and thus their respective scavenging distances would increase.

The above calculations were only applied to laurites found within chromites, but we may also apply them to interstitial laurites, specifically the single laurites found in layers G1 and G4, respectively. In sample ST011G1, the measured laurite volume is 1843  $\mu$ m<sup>3</sup> (Tables 4.3 and 4.7, Fig. 4.4) and the  $\overline{V}_{chromite}^{individual}$  is 7.85 x 10<sup>6</sup>  $\mu$ m<sup>3</sup> (Table 4.4). In sample ST011G4, the measured laurite volume is 1846  $\mu$ m<sup>3</sup> (Tables 4.3 and 4.7, Fig. 4.4) and the  $\overline{V}_{chromite}^{individual}$  is 2.13 x 10<sup>6</sup>  $\mu$ m<sup>3</sup> (Table 4.4). By applying Equation 15, we obtain a  $V_{chromite}^{hypothetical}$  of 3.07 x 10<sup>9</sup>  $\mu$ m<sup>3</sup> for sample ST011G4. The  $N_{scavenged chromites}$  thus is ~ 390 for sample ST011G1 and ~ 1445 for sample ST011G4 (here most likely less as the

chromite count is overestimated). These values fall within the range of chromites needed for laurites found within chromites (Table 4.10).

#### 4.8.3.3. Diffusion of Ru through chromite

Laurite growth to our measured volumes, or the BMS-to-laurite transformation that scavenges Ru from a host chromite (Barnes et al., 2016), with no contribution from the silicate melt and/or BMS melt, necessitates Ru diffusion. Prichard et al. (2017) calculated that it would take 100 years to diffuse Ru through 1 mm of chromite at 800 °C. However, at that time the authors lacked accurate 3D volumes and diffusion coefficients (D) for Ru diffusion in chromite, so  $Cr^{3+}$  was used as a proxy for  $Ru^{3+}$  (log  $D_{Cr} = -17.96 \text{ m}^2/\text{s}$  for 800 °C from Sun, 1958). Zhukova et al. (2018) measured the diffusion of IPGE (in their case Ir, Ru and Rh) in olivines and spinels and reported diffusion coefficients for Ru in spinels at 1300 °C of log D = -17.10to -16.85 m<sup>2</sup>/s  $\pm$  0.2. The temperature value of 1300 °C is when chromite is the first liquidus phase for a chromite-saturated basaltic melt (Ulmer, 1969). Using Zhukova et al.'s (2018) diffusion coefficient, we calculated the Ru diffusion time for three scenarios (Table 4.11): I)  $t_{host \ chromite}^{Ru \ diffusion}$ : how long it would take Ru to diffuse through a measured natural host chromite to form the maximum possible laurite  $(V_{laurite}^{calculated})$ , II)  $t_{scavenged chromites}^{Ru diffusion}$ : how long it would take Ru to diffuse through the necessary number of chromites  $(V_{chromite}^{hypothetical})$  to form the measured natural laurite  $(V_{laurites}^{measured})$ , without accounting for chromite mineral boundaries, and III) the same as II but accounting for the time it takes for the rim and interior of a chromite to equilibrate.

We modelled spherical diffusion, given for a fixed surface concentration and an initially homogeneous sphere with constant diffusivity (MATLAB code, written by DRB, presented in Supplementary material 4.3). A sphere was chosen as isometric chromites have equant volumes (Fig. 4.8), which we can transform to equivalent sphere volumes. To obtain the solutions for time, we combined Equation 6.19 from Crank (1975), here presented as Equation 17, and Equation 8.6.7 from Alberède (1996), here presented as Equation 18.

$$\frac{C_c - C_i}{C_r - C_i} = 1 + 2 \sum_{n=1}^{\infty} -1^n \exp \frac{-D n^2 \pi^2 t}{r^2}$$
(17)

In Equation 17 C<sub>c</sub> is the Ru concentration at the center of the sphere (given by the limit at  $x \rightarrow$  0), C<sub>i</sub> is the initial concentration of Ru (0.414 ppm was used based on Ru content in natural chromites – Barnes et al., 2016 and references therein), C<sub>r</sub> is the concentration at the sphere surface, D is the diffusion coefficient in m<sup>2</sup>/s, n is number of terms used in the summation, t is time in seconds (s) and r is radius in meters (m).

$$\bar{C}(t) = \frac{6 C_c}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 \pi^2 \frac{D t}{r^2}\right) \quad (18)$$

In Equation 18  $\overline{C}$  is the mean Ru concentration of the sphere, while other terms correspond to Equation 17 (in Albarède's (1996) original Equation 8.6.7., C<sub>c</sub> is expressed as C<sub>0</sub> and r is expressed as a). We have used Equation 17 to obtain the value of C<sub>c</sub>, which we inserted in Equation 18 to model how  $\overline{C}$  changes with time.

We solved for time for the first two above mentioned scenarios (Table 4.11):

- It would take 20 to 250 years for the Ru in the host chromite to diffuse and form a laurite of the calculated maximum volume (smaller than the real measured laurite volume as the laurite volume would depend entirely on the chromite volume).
- II) It would take 150 to 800 years for ~ 35 to ~ 700 chromites to be scavenged for Ru to grow to a real measured laurite volume (250 to ~ 2000  $\mu$ m<sup>3</sup>), if we disregard grain boundary diffusion. For sample ST010B4, with smaller chromites and a large laurite (~ 1900  $\mu$ m<sup>3</sup>), would take 800 years and ~ 1500 chromites.

**Table 4.11.** Times for Ru diffusion within chromites. t = time in years. The first row refers to time needed to obtain the calculated (maximum) laurite volume from a single host chromite. The second row refers to time needed for a measured (real) laurite to grow by diffusion through multiple chromites. The third row matches the second, but accounting for equilibration between chromite rims and interiors.

Sample	ST010B4	ST003H		ST014I		ST001J1			
t <sup>Ru</sup> diffusion thost chromite (y) for V <sup>calculated</sup> laurite	30	100	50	100	35	75	250	50	20
t <sup>Ru</sup> diffusion t <sub>scavenged</sub> chromites (y) for V <sup>measured</sup> (no grain boundary)	800	800	200	200	500	400	200	150	150
<ul> <li>t<sup>Ru</sup> diffusion scavenged chromites</li> <li>(y) for V<sup>measured</sup> laurite</li> <li>(interior and rim</li> <li>equilibrated)</li> </ul>	3.86 x 10 <sup>5</sup>	4.03 x 10 <sup>5</sup>	1.07 x 10 <sup>5</sup>	1.02 x 10 <sup>5</sup>	1.99 x 10 <sup>5</sup>	1.28 x 10 <sup>5</sup>	9.17 x 10 <sup>4</sup>	6.45 x 10 <sup>4</sup>	6.78 x 10 <sup>4</sup>

In a monophase crystalline aggregate, such as our chromites, diffusion will first start along grain boundaries. Grain boundary diffusion will no longer significantly contribute, i.e., a uniform diffusion front will propagate through the aggregate once the rim and the interior of the minerals equilibrate (Dohmen and Milke, 2010, and references therein). Regardless of the mineral size, this will occur when (Eq. 19; Mishin and Herzig, 1995):

$$t \ge 150 \ \frac{d^2}{D_l} \qquad (19)$$

In Equation 19 t is time in seconds, d is mineral grain size, in our case the scavenging distance, and D<sub>1</sub> is the single crystal lattice diffusion coefficient. For d we have used  $r_{scavenging}$  in meters (Table 4.9) and for D<sub>1</sub> we have used log D = -17.10 m<sup>2</sup>/s from Zhukova et al. (2018). We calculate that it would take between 55 k and 403 k years for sufficient Ru to diffuse to the measured laurite volumes. Our results are significantly different from Prichard et al.'s (2017) estimate of 100 years, which were based on Cr<sup>3+</sup> diffusion from Sun (1958) of log D<sub>Cr</sub> = - 17.96 m<sup>2</sup>/s for 800 °C, as we used newly available high temperature diffusion coefficients (Zhukova et al., 2018) and applied them to real 3D measured laurite and chromite volumes. The diffusion calculations are all done for 1300 °C, so they do not account for cooling. As diffusion slows with cooling, our estimates represent the quickest possible scenario. Since the Peridotite Zone cooled for 1 Ma after emplacement (Wall et al., 2010; Wall et al., 2018), our longest result of ~ 400 k years would be feasible and there would be time for even larger laurites than the ones observed in this study to form.

#### 4.8.4. Revision of laurite to chromite count ratios

Barnes et al. (2016) and Pagé and Barnes (2016) argued that if the chromites are the principal source of Ru, then every 1-mm sized chromite could contain a laurite. Since the laurites are so small (~10  $\mu$ m), not seeing a laurite in every chromite observed in polished

sections (2D) does not mean the laurite is not present, it could be under the surface in a 30  $\mu$ mthick thin-section, or ground away during sample preparation. Our X-ray  $\mu$ CT results show fewer, but larger than predicted, laurites, leading to a 1:460 laurite to chromite count ratio (albeit overestimated). However, we could have missed laurites below the spatial resolution used (~ 4  $\mu$ m) or erred in excluding those  $\leq$  30  $\mu$ m<sup>3</sup>.

To examine the 1:1 laurite to chromite ratio hypothesis, we apply it to our measured laurite and chromite volumes. Barnes et al. (2016) and Pagé and Barnes (2016) based their hypothesis on a 1 x  $10^9 \,\mu\text{m}^3$  chromite, a volume 200x larger than our average chromite volume (5.02 x  $10^6 \,\mu\text{m}^3$ ). We use the smallest reported laurite volumes, our measurements of the numbers of laurite and chromite crystals, and mass balance equations to investigate if each chromite could host a laurite, what would be its size and could we detect them, and would they significantly contribute to the IPGE + Rh budget.

The smallest reported laurites thus far are 1 x 1  $\mu$ m<sup>2</sup> (in 2D by SEM, Prichard et al., 2017). For simplicity, we will assume a 1  $\mu$ m<sup>3</sup> volume. Applying Equation 15, a 1  $\mu$ m<sup>3</sup> laurite could form in a 1.67 x 10<sup>6</sup>  $\mu$ m<sup>3</sup> chromite, or larger (for simplicity we do not consider multiple chromites contributing towards a single laurite volume, as discussed above). The average individual chromite volume, albeit underestimated (see discussion above), across all samples is 5.02 x 10<sup>6</sup>  $\mu$ m<sup>3</sup> and the minimum is 2.06 x 10<sup>6</sup>  $\mu$ m<sup>3</sup> (Table 4.4), so there are multiple suitable chromite candidates that could host 1  $\mu$ m<sup>3</sup> laurites. We would not detect such laurites as a single voxel in this study is ~ 10  $\mu$ m<sup>3</sup>, and we did not use synchrotron radiation. The average total laurite volume across all samples is 1.22 x 10<sup>3</sup>  $\mu$ m<sup>3</sup> (Table 4.3) and 0.4 % (the volume of discarded  $\leq$  30  $\mu$ m<sup>3</sup> objects) of that average is ~ 5  $\mu$ m<sup>3</sup>. By this estimation, considering laurites have minimum volume of 1  $\mu$ m<sup>3</sup>, we have discarded five laurites.

However, the absence of evidence of laurites smaller than  $1 \,\mu m^3$ , does not signify these do not exist, and we can investigate how small laurites could be to still uphold the 1:1 laurite

to chromite ratio, assuming all undetected laurites are within chromites, not between them. If our total laurite volume error is 0.4 %, which would need to be distributed across 1059 chromites (the average number of chromite crystals in our samples, Table 4.4), each chromite could host a 0.01  $\mu$ m<sup>3</sup> laurite. If we apply our largest laurite volume underestimation of 19 % (based on measured IPGE + Rh content, Table 4.6), which equals 232  $\mu$ m<sup>3</sup>, and distribute it across 1059 chromites, each chromite could host a 0.22  $\mu$ m<sup>3</sup> laurite.

It is clear that laurites of sizes comparable to  $0.01 \ \mu m^3$ ,  $0.1 \ \mu m^3$  or even  $1 \ \mu m^3$ , would be extremely difficult to identify by most readily available 2D or 3D methods, but we cannot claim they are not there. Thus, we can neither confirm nor deny the 1:1 laurite to chromite ratio hypothesis. Importantly, such small laurite volumes do not represent a significant contribution to the overall IPGE + Rh sample budget.

### 4.9. Conclusions

The application of laboratory-based high-resolution X-ray computed microtomography to samples of chromitite layers from the Stillwater Complex allowed precise measurement of both laurite and chromite volumes. We combined these parameters with whole rock geochemistry, mass balance and diffusion calculations and found:

I. The 3D laurite volumes are systematically larger than previously reported 2D laurite sizes. An unsurprising find due to the limitations of the 2D analysis of 3D objects, but with important implications for laurite-chromite calculations. The 3D laurite location is in line with previous 2D observations; there are more laurites within chromites than between chromites. All chromite-hosted laurites are located 20-30  $\mu$ m from the chromite-silicate interface.

- II. Few large laurites account for most of the IPGE + Rh budget in samples many times their volume.
- III. Chromite cumulate pile formation through chromite sinking, layer settling and compaction, took between 65 and 30 k years. The latest reported Peridotite Zone cooling estimates are 1 Ma.
- IV. Laurites crystallizing from a silicate melt after the formation of the chromite cumulate pile would need between 100x – 6500x the amount of silicate material now present in the sample. Silicate melt percolation between closely packed chromites, with liquid fractions (porosities) between 0.11 - 0.36, was efficient as the slowest estimate of necessary silicate melt volumes percolation times are less than 10 hours.
- V. Single chromites, hosts to laurites, do not hold sufficient Ru to account for the laurite volumes. Laurites would need to scavenge Ru from between ~ 40 and ~ 1500 surrounding chromites to obtain sufficient Ru. For only one identified laurite-chromite pair was the host chromite large enough to be the sole Ru supplier.
- VI. The measured host chromites would quickly be exhausted of Ru, as Ru would diffuse through a single chromite during 20 to 250 years.
- VII. Ru diffusion through multiple neighboring chromites would take 150 to 800 years, to obtain sufficient Ru for laurites to grow to their measured volumes (without accounting for chromite grain boundary diffusion).
- VIII. Allowing the chromite interior and grain boundary to equilibrate, diffusion of sufficientRu for laurites to grow to their measured volumes would take ~ 65 k to ~ 400 k years.

Based on the number, size, and location of laurites, we favor the laurite formation model by Barnes et al. (2016). If the model proposed by Finnigan et al. (2008) was the principal one, where the melt is the main source of Ru, we would expect to find many minute laurites at the chromite-silicate interface or within chromites, but close to the chromite-silicate interface. Direct crystallization from the melt cannot be entirely disregarded as we have shown that there was sufficient melt available to supply the Ru necessary for laurite nucleation at the chromitemelt interface and subsequent laurite and growth. However, we have found few large and dispersed laurites, located both within and in-between chromites. Our diffusion calculations have shown that there was sufficient time for a diffusive exchange between chromites and BMS, to form a laurite, and thus we favor chromites as the principal source of Ru and the model of laurite formation by Barnes et al. (2016).

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# 4.11. Supplementary material

**Supplementary material 4.1.** Two-dimensional measurements of laurites from Prichard et al. (2017). The minimal and maximum axes are averaged for all laurites in a single layer. The intermediate axis is calculated as the average value between the minimal and maximum axis. The measure of the three axes is used to calculate an ellipsoid volume.

	Number of laurites	Average min axis (µm)	Intermediate axis - calculated (µm)	Average max axis (µm)	Volume (µm <sup>3</sup> )
Layer K	13	3.9	4.7	5.5	420
Layer J	11	4	4.65	5.3	410
Layer I	5	4	4.5	5	370
Layer H	21	3.7	4.15	4.6	280
Layer G	36	3.5	3.75	4	220
Layers C+E	7	2.7	2.8	2.9	90
Layer B	39	2.7	3.1	3.5	120
Layer A	4	2.3	2.45	2.6	60
Average	17	3.35	3.76	4.17	250
Min	4	2.3	2.45	2.6	90
Max	39	4	4.7	5.5	420

**Supplementary material 4.2.** Images and semi-quantitative chemical data obtained by SEM of the 2D plane within sample ST003H containing the targeted laurite.





Spectrum label	Spectrum 1	Spectrum 2	Spectrum 3
Ir	4.35	4.34	4.31
Os	7.98	7.93	7.56
Ru	43.38	45.87	41.42
S	35.78	36.65	34.64
Total	91.49	94.79	87.93

## Supplementary material 4.3. MATLAB code, written by DRB, used to calculate Ru

diffusion for laurites located within chromites.

\_\_\_\_\_

%DiffusionSpherical\_1.m

%Written by D.R. Baker, McGill University, January 2022

%Designed to investigate diffusive loss by spherical diffusion from an

%initially homogeneous sphere

%

% Based upon Eqn 6.19 of Crank (1975) and Albarede (1995)

%C1--initial uniform concentration

%Co -- constant surface concentration

clear all

C1 = 0.414e-6;% original ppm in chromite--Marko use 0.414 ppm, max from Locmelis et al. (2011) is 0.5 ppm;

Co = 0; %Boundary maintained at 0 concentration

a = 0.0001486; % chromite grainsize - radius of chromite grain (m) Loferski et al.(1990 USGS Bull.):0.00005, Barnes et al. (2016):0.00086 (m)

D = 1e-17; %diffusivity (m^2s^-1) at 1300 oC, from Zhukova et al. (2018)

```
DpisquaredOverasquared = (D*pi^2/a^2);
```

```
DOverasquared = (D/a^2);
```

time = 0; % time in year

i=0;

while time< 200.1 % time in years

i=i+1;

time = time+0.1;

t(i) = time;

tsec = t(i)\*365.25\*24\*3600;

%concentration at centre

n = 0;

Summ = 0;

```
SummOld = 10;
```

Diff = abs(Summ-SummOld);

while Diff > 0

SummOld=Summ;

n = n+1;

Summ = Summ + ((-1)^n)\*exp(-DpisquaredOverasquared\*n^2\*tsec);

```
Diff = abs(Summ-SummOld);
```

end

```
Ccentre(i) = (C1+(Co-C1)*(1+2*Summ));
```

% Mean concentration of the sphere during diffusive loss (Albarede Eqn 8.6.7)

n = 0;

Summ = 0;

SummOld = 10;

Diff = abs(Summ-SummOld);

while Diff > 1e-6

SummOld=Summ;

n = n+1;

Summ = Summ +  $(1/n^2)^{exp(-n^2*pi^2*((D^{tsec})/a^2))};$ 

Diff = abs(Summ-SummOld);

end

```
Cmean(i) = 6*C1/pi^2 * Summ;
```

%.....

```
% Ru, Chromite, and Laurite Specific calculations
```

```
% Assumes all Ru diffuses to the surface of the sphere and forms a single
```

% crystal

rhoChromite = 4.8e3; %kg/m^3 Palache et al 1944

rhoLaurite = 6.43e3; %kg/m^3 Bowles et al 1983

rhoRu = 12.1e3;%kg/m^3

MWLaurite = 165.2; %g/mol web minerals

MWRu = 101.1; %g/mol

```
MassFracRuInLaurite = 0.6067; % webminerals
%TotalLost(i) = 4/3*pi*a^3*rhoChromite(C1-Cmean(i));
TotalMassRuLost(i) = (C1-Cmean(i))*rhoChromite*4/3*pi*a^3;
TotalMassLaurite(i) = TotalMassRuLost(i)/MassFracRuInLaurite;
TotalLauriteVolume(i) = TotalMassLaurite(i)/((4/3)*pi*rhoLaurite);
TotalLauriteDimension(i) = (TotalLauriteVolume(i))^(1/3);
%.....
end
ChromiteVolume = 4/3*a^3 % m^3
TotalInitialRu = C1*rhoChromite*4/3*pi*a^3
%figures ......
figure (1)
plot(t,Ccentre,'x')
```

title('Concentration at centre')

xlabel('time (years)')

ylabel('CoChromiteVolume = 4/3\*a^3 % m^3ncentration at centre')

figure (2)

plot(t,Cmean)

title ('Mean concentration of sphere')

xlabel('time (years)')

ylabel('Mean concentration of sphere')

figure (3)

plot(t,TotalMassRuLost)

title ('Total mass of Ru lost')

xlabel('time (years)')

ylabel('Total mass of Ru lost (kg)')

figure (4)

plot(t,TotalLauriteVolume)

title ('Characteristic Laurite Volume') xlabel('time (years)') ylabel('Characteristic laurite volume (m^3)') figure (5) plot(t,TotalLauriteDimension) title ('Characteristic Laurite length') xlabel('time (years)') ylabel('Characteristic laurite length (m^3)')

## Chapter 5

### Conclusions

In this thesis, specific concentration processes of PGE have been studied.

The formation of Pt micro nuggets is an important topic due to nugget formation being a hinderance in studies of PGE partitioning, solubility and diffusion. In order to study the formation of Pt micro nuggets with X-ray computed microtomography ( $\mu$ CT) we built and tested an induction furnace at the third generation Elettra synchrotron in Trieste (Italy). The furnace was needed due to the unavailability of the high temperature environmental devices with precise temperature and oxygen fugacity control. We were able to achieve temperatures up to 1450 °C with the error of ± 5 °C and high spatial resolution. The furnace is still in development with further advances coming in the near future.

We were able to achieve oxygen fugacity control in the furnace by altering the susceptor size and configuration. We used a configuration that imposes an oxygen fugacity gradient to the top of the sample to study Pt nugget formation. Nuggets either form by rapid cooling (quench) or by direct crystallization from the melt due to the oxygen fugacity change. We show that it is unlikely that the nuggets form at quench given the short time available and that they do form in the area of the imposed lower fugacity gradient. The effect is more pronounced at higher temperatures, which is to be expected. Increased numbers of small nuggets in the area of the fugacity gradient show that the nuggets indeed form as a stable phase at high temperature. As such, they can be excluded from the partitioning, solubility and diffusion experiments. X-ray  $\mu$ CT can help in identifying and targeting areas of the sample that are nugget free for geochemical analysis. Interestingly, as nuggets form at high temperature they can serve as a transport mechanism for PGE as they have been found in natural systems.

This thesis also reports my study of the formation of laurite near chromite by direct crystallization or diffusive replacement of BMS in chromite. Using a nondestructive X-ray three-dimensional (3D) imaging approach we have found that laurites are larger than previously reported by two-dimensional (2D) techniques and account for all the Ru in the sample. If the laurites are formed by direct crystallization they would need 100x to 6500x the silicate material available to them today, this material could be available if the percolation was efficient enough. Single chromites do not hold enough Ru to account for the laurite formation and it would take 40 to 1500 surrounding chromites to account for the laurite size. Given the available diffusion coefficients and multiple mineral grain boundaries needed to be crossed for enough Ru to diffuse, 65 k to 400 k years is necessary to form the laurite.

Our findings offer a tentative conclusion that the most probable laurite formation process is Ru diffusion through chromite grains. This is supported by the number, location, and size of laurites found. However, we cannot entirely dismiss the possibility that laurite crystallized directly from the melt, as there was time for sufficient melt to percolate. In order to fully support our tentative conclusion, we propose future work to be done on Ru diffusion in melt. This would allow constraints to be put on laurite growth from the melt and thus likely resolve the issue. Additional X-ray mCT, targeting large laurites, and consecutive sectioning of those laurites, would allow more robust Os isotopic studies that would answer the question of Os provenance, determining whether the Os isotopic ratio is closer to mantle or crustal sources and thus provide additional information on laurite formation. Past studies in the Os isotopic composition of the laurite in and in-between the chromite minerals have been hampered by the small size of the laurite grains found and used for the analysis. Larger laurites would provide more material for analysis and thus more accurate determination of Os isotopic composition.