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Origine et évolution des éléments volatils accrétés par les corps planétaires du système solaire interne

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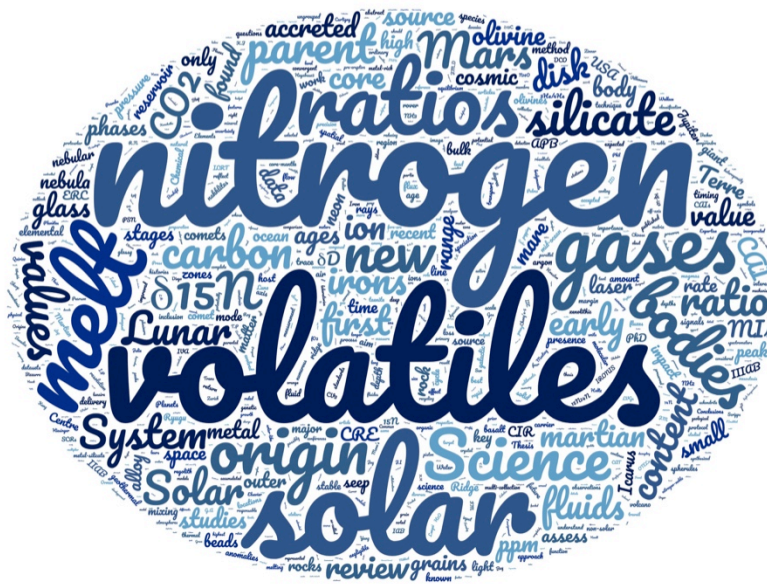
Habilitation à Diriger des Recherches (HDR) à l'Université de Lorraine

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Chargée de recherche CNRS (CRCN)

Centre de Recherches Pétrographiques et Géochimiques (CRPG, CNRS-UL)

Origine et évolution des éléments volatils accrétés par les corps planétaires du système solaire interne



29 novembre 2022

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1 – Synthèse des activités de recherche, d'enseignement et d'administration

Mes travaux de recherche portent sur l'origine des éléments volatils accrétés par les corps planétaires du système solaire interne ainsi que sur leurs comportement, distribution et inventaire dans les réservoirs profonds. Je m'intéresse particulièrement à l'utilisation des signatures isotopiques des gaz rares (hélium, néon, argon), de l'hydrogène, du carbone et de l'azote comme traceurs de sources de volatils et de processus géochimiques ou cosmochimiques. Pour mieux comprendre quand et comment notre planète a accru les éléments légers essentiels à l'émergence de la vie, j'analyse, en utilisant différentes approches géochimiques, des échantillons volcaniques terrestres, des météorites, des échantillons rapportés sur Terre par les missions spatiales ainsi que des échantillons synthétiques.

1.1 – Éducation et parcours professionnel

- 2014 – présent Chargée de recherche de classe normale, CNRS
Centre de Recherches Pétrographiques et Géochimiques, FR
- 2010 – 2014 Chercheuse postdoctorale
Centre de Recherches Pétrographiques et Géochimiques, FR
- 2004 – 2010 Ph.D. in Earth Sciences
Scripps Institution of Oceanography, University of California San Diego, USA
- 1999 – 2004 dipl. sc. nat. ETH (*Master of Science ETH*)
Département des Sciences de la Terre, École Polytechnique Fédérale de Zurich, CH

Au cours de mes **études en Sciences de la Terre** à l'École Polytechnique Fédérale de Zurich (ETH), j'ai commencé à m'intéresser à la géochimie isotopique; pour mon projet de fin d'étude, j'ai analysé par spectrométrie de masse la composition isotopique du chlore et de l'oxygène dans des fluides géothermaux que j'ai échantillonnés en Islande afin de retracer les sources et le cycle de ces fluides. En octobre 2004, j'ai commencé mon **doctorat (PhD) en Sciences de la Terre** à la Scripps Institution of Oceanography (SIO), University of California San Diego (UCSD) sous la direction de David Hilton. Alors que la première année du parcours doctoral était consacrée à la formation via des cours obligatoires (principalement en océanographie géologique, chimique, physique et biologique) et à l'examen de qualification, j'ai ensuite analysé les gaz rares et le carbone (CO₂) dans divers échantillons terrestres (solides, fluides, gaz) pour mieux comprendre l'origine, le cycle et le comportement de ces éléments volatils dans différents contextes géologiques. Après avoir soutenu ma thèse en mars 2010, j'ai souhaité élargir mes domaines d'intérêt ainsi que mes champs de compétences dans l'optique d'avoir une vision plus large sur l'origine, la distribution et l'évolution des éléments volatils dans le système solaire. A cette fin, j'ai obtenu une **bourse postdoctorale** de deux ans du Centre National d'Études Spatiales (CNES) pour analyser au Centre de Recherches Pétrographiques et Géochimiques (CRPG) les gaz rares légers piégés dans les échantillons cométaires amenés sur Terre par la mission *Stardust* de la NASA. En parallèle de ces travaux effectués par spectrométrie de masse gaz rares, je me suis formée à l'utilisation de la spectrométrie de masse à ions secondaires pour

analyser des météorites ainsi que des échantillons lunaires collectés lors des missions *Apollo*. Grâce à mes collaborations avec Bernard Marty, j'ai aussi commencé à m'intéresser davantage aux variations isotopiques de l'azote dans le manteau terrestre et dans divers objets et réservoirs du système solaire (une fois que j'avais compris que le mot français *azote* désigne l'élément chimique que je ne connaissais que sous le nom *Stickstoff* ou *nitrogen* avant mon arrivée au CRPG). En 2014, j'ai obtenu un poste de **chargée de recherche CNRS** au CRPG. En reconnaissance de mes premiers travaux en géochimie et cosmochimie, j'ai reçu la **médaille de bronze du CNRS** en 2017. Cette distinction représentait un encouragement important de la part du CNRS alors que je développais une carrière de chercheuse indépendante et que je mettais en place ma propre équipe de recherche au début de mon projet **ERC-2016-STG 'VOLATILIS'** - *Origin of volatile elements in the inner Solar System* (1er février 2017 - 31 juillet 2022). Le financement de mon projet 'VOLATILIS' m'a permis de co-encadrer deux doctorants (Julien Boulliung et Cécile Deligny), qui poursuivent maintenant leurs carrières scientifiques en postdoc, et une chercheuse postdoctorale (Celia Dalou), qui a obtenu un poste de chargée de recherche CNRS au CRPG en 2021. Par ailleurs, pendant plus de 5 ans, j'ai pu me concentrer sur la science à plus haut risque plutôt que sur la recherche de financements. Les résultats de mes travaux ont été publiés dans **45 articles** (+7 articles supplémentaires qui sont actuellement en cours de révision ou acceptés pour publication) dans des revues internationales à comité de lecture et présentés lors de nombreuses conférences et ateliers nationaux et internationaux.

- **1330** citations (Google Scholar)
- h-index **20** (Google Scholar)
- 10 présentations en séminaires invités d'instituts de recherche nationaux et internationaux
- 2 présentations "keynote" (2016, 2020) + 1 présentation invitée (2021) à la *Goldschmidt Conference*
- Présentations invitées au *European Lunar Symposium* (2014), *Nu Instruments webinar* (2021), *23rd International Mineralogical Association General Meeting* (2022)
- 31 présentations orales et 3 présentations poster en conférences, ateliers et écoles thématiques (en tant que première autrice et présentatrice, depuis 2010)

Depuis mon arrivée au CRPG, j'ai abordé différentes problématiques scientifiques liées à l'origine des éléments volatils (hydrogène, carbone, azote) sur Terre et la chronologie de leur accréation par différents corps planétaires formés au sein du système solaire interne. Pour mener à bien ces recherches, qui font principalement partie du thème "Cosmochimie et Planétologie" du CRPG, j'ai mis en œuvre une grande variété de techniques d'observation et de quantification, et j'ai fortement contribué au **développement de nouvelles méthodologies analytiques**. Je suis affiliée à la fois à la plateforme instrumentale "Spectrométrie Gaz Rares" et à la plateforme "LG-SIMS-Nancy", étant donné que mon approche analytique consiste à utiliser deux techniques de pointe – la spectrométrie de masse gaz rares et la spectrométrie de masse à ions secondaires – pour étudier les éléments volatils dans les échantillons terrestres, extraterrestres et synthétiques. Un montage financier comprenant un

apport du CPER OTELo et de mes ressources propres banalisées (*overheads* de mon ERC 'VOLATILIS') m'a permis d'acquérir et d'installer un nouveau spectromètre de masse statique (Noblesse HR) et un nouveau système de chauffage laser (MIR 10) sur la plateforme "Spectrométrie Gaz Rares". J'ai ensuite développé les nouveaux protocoles d'acquisition de données en multi-collection qui ont amélioré la précision des analyses couplées azote–gaz rares d'échantillons de petites tailles comme ceux amenés sur Terre par les missions spatiales (*Apollo, Hayabusa2*). En parallèle, sur la plateforme "LG-SIMS-Nancy", j'ai développé une nouvelle approche pour analyser l'azote *in situ* dans des silicates, ce qui me permet maintenant de cibler des échantillons de taille micrométrique tels que les inclusions vitreuses dans les échantillons terrestres et extraterrestres ainsi que les phases vitreuses dans les échantillons synthétiques. Grâce à ces avancées j'ai aussi pu établir, au cours de ces dernières années, des **collaborations nationales et internationales**, notamment avec des chercheurs de l'Institut des Sciences de la Terre d'Orléans (ISTO), de l'Institut de Planétologie et d'Astrophysique de Grenoble (IPAG), de l'université de Tokyo, du NASA-Johnson Space Center, de l'Université de Münster, de l'Université de Bayreuth et du GEOMAR Helmholtz Centre for Ocean Research. Je tiens aussi à souligner que j'assume, depuis plusieurs années, diverses **responsabilités administratives**: je suis co-responsable scientifique du thème "Cosmochimie et Planétologie" du CRPG, et je suis membre élu du conseil de laboratoire du CRPG et du conseil de pôle scientifique de l'Observatoire Terre et Environnement de Lorraine (OTELo).

Au-delà des avancées scientifiques que je présente dans les chapitres suivants, mon objectif durant cette première partie de carrière était d'acquérir les compétences techniques et administratives pour gérer et mener à bien d'autres projets de grande ampleur dans les années futures. Je suis notamment partenaire (et responsable scientifique au CRPG) de l'ANR PRC (2022) "CLASTS", portée par Lydie Bonal de l'IPAG, qui a pour but d'étudier des xénolites dans des météorites chondritiques via des approches pétrographiques, spectrales, isotopiques et chronologiques pour identifier et caractériser les divers corps parents initiaux de ces xénolites dans le système solaire. J'ai aussi déposé, en mars 2022, un projet ERC-2022-COG 'IRONIS' - *Light elements in irons and metal-rich meteorites: Their isotopic distribution and evolution in the protoplanetary disk*, et je suis invitée à l'audition de la seconde étape en novembre. Alors que l'objectif de ces deux projets est d'étudier de nouveaux types de météorites, je souhaite aussi remettre un pied sur terre et appréhender, plus en détail, le comportement de l'azote pendant la formation, la différenciation et l'évolution de notre planète grâce à l'analyse d'échantillons volcaniques et expérimentaux. Finalement, j'espère pouvoir poursuivre, dans les années futures, des activités d'enseignement et d'administration tout en me concentrant principalement sur mes activités de recherche et d'encadrement et en participant activement au travail analytique en laboratoire.

1.2 – Encadrement

- **Romain Benigna** (M1, 2015 – 2016)

L'objectif de ce stage de M1 était de déterminer la composition isotopique de l'azote piégé dans des olivines de basaltes lunaires collectés lors des missions *Apollo*. Malheureusement, le spectromètre de masse gaz rares VG5400 et la ligne de purification associée avaient été gravement contaminés par des hydrocarbures début 2015. Par conséquent, Romain a dû passer la totalité de son stage de recherche à analyser des blancs et des standards d'air, et les échantillons lunaires n'ont pas pu être analysés.

- **Cécile Deligny** (M2, 2017 – 2018)

L'objectif principal de ce projet M2, qui a été co-encadré par Yves Marrocchi, était de réaliser une étude pétrographique et isotopique (oxygène et azote) détaillée de la météorite D'Orbigny. Cécile a étudié la texture et la composition minéralogique/chimique de trois sections polies de la météorite par microscopie électronique à balayage et microsonde électronique. Elle a ensuite déterminé la teneur et le rapport isotopique de l'azote piégé dans les inclusions vitreuses et le verre interstitiel ainsi que la composition isotopique de l'oxygène de diverses phases minérales (olivine, pyroxène, anorthite) par spectrométrie de masse à ions secondaires. Les nouvelles données isotopiques ont fourni des informations clés sur l'origine de D'Orbigny et l'histoire du corps parent des angrites. Plus important encore, les premiers résultats acquis ont servi de base à une étude plus détaillée des angrites dans le cadre de la thèse de doctorat de Cécile au CRPG (voir ci-dessous).

- **Marine Joulaud** (M2, 2020 – 2021)

Ce projet de M2, qui a été co-encadré par Jessica Flahaut, a été réalisé dans le cadre de la Mission lunaire des Émirats (*Emirates Lunar Mission, ELM*). Le Centre spatial Mohammed Bin Rashid (MBRSC) prévoit d'envoyer un rover sur la Lune à la fin de 2022. Jessica Flahaut et moi-même sommes toutes deux membres des groupes de travail en charge de la sélection du site d'alunissage et de la planification de la trajectoire du rover, et nous sommes membres de l'équipe des opérations scientifiques de l'*ELM*. La tâche principale de Marine était d'étudier les caractéristiques géologiques (composition chimique, topographie, distribution des blocs rocheux) des sites d'alunissage principal et secondaires de l'*ELM*. Elle a également effectué des tests préliminaires d'outils de traitement des données qui seront obtenues par les caméras du rover en étudiant des images macro- et microscopiques du régolithe lunaire et de matériaux analogues, dans le but de développer un algorithme de caractérisation automatique des grains (c'est-à-dire la distribution des formes et des tailles de grains). Marine est actuellement doctorante à l'Université de Lyon.

- **Julie Gamblin** (M2, 2021 – 2022)

Dans le cadre de ce projet de M2, qui a été co-encadré par Béatrice Luais, Julie a étudié la teneur et la composition isotopique de l'azote piégé dans diverses pallasites. L'origine de ces météorites mixtes, composées principalement d'olivine et d'un alliage fer-nickel, reste controversée. L'analyse par spectrométrie de masse gaz rares de fragments de métal et de grains d'olivines provenant de pallasites dites "carbonées" et "non-carbonées" a amélioré notre connaissance de la distribution et de la variation isotopique de l'azote dans le disque protoplanétaire, et les données ont fourni de nouvelles informations sur les liens génétiques entre différentes pallasites et les météorites de fer. En attendant d'être sélectionnée pour un projet doctoral, Julie va continuer à travailler sur ce projet sous ma direction en tant qu'assistante ingénieur (AI) pendant un an (à partir d'octobre 2022).

- **Julien Boulliung** (PhD, 2017 – 2020; Co-encadrement avec Yves Marrocchi)

L'objectif de la thèse "Solubilité, spéciation et diffusion de l'azote dans les verres et silicates fondus" était d'étudier les processus sous-jacents affectant l'abondance et la composition isotopique de l'azote dans les phases vitreuses d'échantillons terrestres et extraterrestres en utilisant une combinaison de techniques analytiques, telles que la spectrométrie de masse gaz rares, la spectrométrie de masse à ions secondaires et la spectroscopie Raman (ainsi que la microscopie électronique à balayage et la microsonde électronique). Plus précisément, la solubilité, la spéciation et la diffusion de l'azote dans les silicates fondus et/ou les verres ont été étudiées par une approche expérimentale et analytique ciblée. Les résultats de ces travaux sont discutés dans deux articles publiés dans des revues internationales à comité de lecture (Boulliung et al., *GCA*, 2020; Boulliung et al., *Am. Mineral.*, 2021). En parallèle, Julien a été fortement impliqué dans le développement analytique sur le spectromètre de masse gaz rares Noblesse HR (Zimmermann et al., en cours de rédaction), et il a collaboré avec Célia Dalou sur le développement d'expériences au piston cylindre pour étudier le comportement de l'azote lors du partage métal-silicate (Dalou et al., *PNAS*, 2019). Julien est désormais chercheur postdoctoral au département des Sciences de la Terre de l'Université d'Oxford.

- **Cécile Deligny** (PhD, 2018 – 2021; Co-encadrement avec Etienne Deloule)

L'objectif de la thèse "Origine des éléments volatils et chronologie de leur accréation au sein du système solaire interne : Apport de l'analyse *in situ* des achondrites" était d'étudier l'abondance des éléments volatils (azote, hydrogène) et leurs rapports isotopiques ($^{15}\text{N}/^{14}\text{N}$ and D/H) dans diverses achondrites, telles que les angrites, les météorites martiennes et les aubrites. Comme les corps parents de ces objets se sont accrétés au cours des premières étapes de la formation des planètes, les signatures isotopiques de l'azote et de l'hydrogène piégés dans des inclusions vitreuses peuvent fournir des informations clés sur l'évolution la plus précoce des volatils planétaires, et elles peuvent améliorer notre compréhension de l'origine et la chronologie d'accréation des éléments volatils sur la Terre et d'autres corps planétaires. Les résultats des analyses des angrites et des météorites martiennes sont discutés dans deux articles scientifiques (Deligny et al., *GCA*, 2021; Deligny et al., *GCA*, en cours de révision). Parallèlement aux analyses des achondrites, Cécile a contribué aux analyses de l'azote dans d'autres échantillons naturels et synthétiques en réglant la microsonde ionique au début de plusieurs sessions analytiques (Dalou et al., *PNAS*, 2019; Füre et al., *Chem. Geol.*, 2021; Dalou et al., *GPL*, 2022; Fukuyama et al., *EPSL*, en cours de révision). Cécile est maintenant chercheuse postdoctorale à la Freie Universität Berlin.

- **Célia Dalou** (Chercheuse postdoctorale, 2017 – 2021)

Grace à mon projet ERC 'VOLATILIS', la plateforme "Cosmochimie et Magmatologie Expérimentale" du CRPG a pu être équipée d'une cellule hydrothermale à enclume de diamant (HDAC). En utilisant la HDAC, Célia a établi un nouveau protocole pour des études *in situ* par spectroscopie Raman de fluides et silicates fondus riches en azote à haute pression et haute température (Dalou et al., *Front. Earth Sci.*, 2022). Un nouveau piston cylindre, installé récemment au CRPG, a permis à Célia de poursuivre ses travaux sur le fractionnement isotopique de l'azote pendant le partage métal-silicate (c'est-à-dire la formation du noyau planétaire; Dalou et al., *PNAS*, 2019) et le dégazage d'un océan magmatique (Dalou et al., *GPL*, 2022) afin de mieux comprendre comment les processus de différenciation planétaire ont pu modifier la composition isotopique de l'azote du manteau terrestre au cours de son évolution. En 2021, Célia a obtenu un poste de chargée de recherche CNRS au CRPG.

1.3 – Sources de financement

| | |
|------|--|
| 2017 | H2020-EU.1.1. – EXCELLENT SCIENCE – European Research Council (ERC) ERC-2016-STG 'VOLATILIS' – 1 396 300 € Origin of volatile elements in the inner Solar System |
| 2016 | Programme National de Planétologie (PNP, INSU) – 5 500 € Volatile abundance and isotope analyses of lunar melt inclusions |
| 2016 | Conseil régional de Lorraine – 20 003 € Origine et évolution des éléments volatils dans le système Terre-Lune |
| 2015 | Programme National de Planétologie (PNP, INSU) – 10 000 € Coupled H- and N-noble gas analyses of lunar basalts: Constraints on the origin and evolution of volatiles in the Earth-Moon system |

1.4 – Enseignement

Pendant mon doctorat à la Scripps Institution of Oceanography, j'ai encadré chaque année des travaux dirigés pour des étudiants de premier cycle à la University of California San Diego dans le cadre des cours *The Earth*, *Geology of National Parks* et *Environmental Perils*. Depuis mon recrutement au CNRS, j'ai enseigné tous les ans un cours magistral et j'ai encadré des travaux dirigés en géochimie à l'École Nationale Supérieure de Géologie (ENSG). J'interviens aussi plusieurs fois dans le cadre du Master 2 Terre & Planètes au CRPG, avec un volume horaire annuel compris entre 25 et 30 heures.

- "**Géochimie**" – Ingénieurs ENSG 2ème année – ~20 heures (CM et TDs)
- "**Introduction à la géochimie des gaz rares**" – Master 2 Terre & Planètes – 3 heures (CM)
- "**Formation et évolution de la Lune**" – Master 2 Terre & Planètes – 3 heures (CM)
Ce cours fait partie du module "Cosmochimie", dont je serai responsable à partir de l'année 2022/23. En tant que responsable du module je vais gérer le planning du module sur une semaine ainsi que l'organisation du partiel.
- "**La course à l'espace**" – Master 2 Terre & Planètes – 2 heures (CM)
Ce cours fait partie du module "Missions spatiales", dont j'étais responsable de 2014/15 à 2021/22.

1.5 – Administration

| | |
|----------------|---|
| 2022 | Membre du comité de recrutement d'un Ingénieur Projets Européens (IPE) à la Délégation Centre-Est du CNRS. |
| 2022 – présent | Membre du comité de pilotage de la NanoSIMS de l'Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), Paris. |
| 2019 – présent | Membre du "Groupe de travail thématique système solaire" (GTSS) du CNES. Le GTSS discute et évalue les activités des laboratoires français associées aux missions spatiales en cours ou à venir. |
| 2019 – 2022 | Membre du "F.W. Clarke Award committee" (Geochemical Society). Ce comité, que j'ai présidé en 2021 et 2022, honore une contribution exceptionnelle en géochimie ou cosmochimie d'un jeune scientifique en début de carrière. |
| 2019 – 2020 | Co-responsable du groupe de travail "Samples and Joint Virtual Laboratory" du CNSA-ESA International Lunar Research Team (ILRT). Ce groupe, composé de chercheurs Chinois et Européens, avait été mis en place par les agences spatiales |

Chinoise et Européenne pour identifier des intérêts communs et définir des objectifs scientifiques potentiels ainsi que les mises en œuvre techniques possibles sur une station de recherche lunaire internationale (et en préparation de celle-ci).

- 2018 – présent **Membre élu du conseil de laboratoire** du CRPG.
- 2017 – présent **Rapportrice** pour des demandes de financement dans le cadre des programmes CNRS INSU Tellus, ERC, FWF (Lise Meitner Programme), NASA-NSPIRES, NERC, NSF, SNSF (Ambizione).
- 2017 – présent **Membre élu du conseil de pôle et d'OSU** OTELo ("Observatoire Terre Environnement de Lorraine") en tant que représentante du sous-collège CRPG, collège B, ainsi que **membre de la commission recherche**. OTELo est un pôle scientifique de l'Université de Lorraine et un Observatoire des Sciences de l'Univers (OSU) qui assure des missions d'animation et de coordination de la recherche, auxquelles s'ajoutent des missions d'observation et de formation.
- 2016 – 2019 **Membre du comité de pilotage scientifique** de la communauté "Reservoirs and Fluxes", Deep Carbon Observatory (DCO, 2009 – 2019). Le DCO regroupait une communauté mondiale de plus de 1000 scientifiques qui cherchait, pendant 10 ans, à mieux comprendre l'origine, l'abondance et l'évolution du carbone sur Terre.
- 2016 – présent **Co-responsable scientifique** du thème "Cosmochimie et Planétologie" (précédemment: "Formation et évolution du système solaire et des planètes") du CRPG. A ce titre, je suis aussi membre du comité de direction du CRPG.
- 2012 – 2017 Responsable des séminaires internes du CRPG.

1.6 – Organisation de conférences et ateliers

- 2021 **Co-organisation** de l'atelier virtuel *DINGUE (Developments In Noble Gas Understanding and Expertise) VII*. L'objectif de *DINGUE* est de discuter des aspects techniques et scientifiques de la géo- et cosmochimie des gaz rares.
- 2019/20/22 **Co-organisation (et co-présidence en 2022)** du *European Lunar Symposium (ELS)*. L'objectif principal de ce colloque est de rassembler la communauté scientifique européenne intéressée par les différents aspects de l'exploration lunaire.
- 2019 **Co-organisation** de l'atelier *DINGUE VI* à Zurich, CH.
- 2018 **Co-organisation** de l'école d'hiver "Volatile elements in the Solar System" aux Houches, FR. Cette école interdisciplinaire – à la frontière entre les sciences planétaires, la chimie du milieu interstellaire et la cosmochimie – s'est concentrée sur l'origine et l'évolution de l'eau et des éléments volatils (carbone, azote et gaz nobles) dans le système solaire primitif.
- 2017 **Co-organisation et co-présidence** de la session "Origin, evolution, and budget of volatiles in the terrestrial planets" à la *Goldschmidt Conference* à Paris, FR.
- 2016 **Co-organisation** de l'atelier *DINGUE IV* au CRPG. Plus de 100 scientifiques du monde entier ont participé à cet atelier organisé en hommage à notre collègue et ami Pete Burnard.
- 2015 **Co-organisation et co-présidence** de la session "Volatiles and the origin of the Moon" à la *Goldschmidt Conference* à Prague, CZ.

1.7 – Activité éditoriale

- 2020 – 2021 **Éditrice invitée** pour le numéro spécial "Earth's Volatile Cycle within the Crust-Mantle System: A volume in memory of Dave Hilton" dans le journal *Chemical Geology*.
- 2018 – 2019 **Éditrice invitée** pour le numéro spécial "Science and Exploration of Lunar Resources with ESA's PROSPECT Package" dans le journal *Planetary and Space Science*.
- 2012 – présent **Relectrice** pour différentes revues internationales à comité de lecture (~6 articles/année): ACS Earth and Space Chemistry, Chemical Geology, Earth and Planetary Science Letters, G-Cubed, Geochemical Journal, Geochemical Perspective Letters, Geochemistry, Geochimica et Cosmochimica Acta, Geology, Marine Geology, Meteoritics and Planetary Science, Nature, Nature Geoscience, Planetary and Space Science, Progress in Earth and Planetary Science, Icarus, Scientific Reports.

1.8 – Jurys de thèses

- 2022 **Marion Auxerre** (Université de Lorraine; **examinatrice**): Cristallisation des olivines dans les chondres barrés et macro-porphyriques
- 2019 **Antonio Caracausi** (Université de Lorraine; **examinatrice**): Noble gases as geochemical tracers of Earth's dynamic and evolution
- 2018 **Sandrine Péron** (Sorbonne Paris Cité; **examinatrice**): Origine des éléments volatils terrestres: apport de la géochimie des gaz rares
- 2017 **Rémi Delon** (Université de Lorraine; **examinatrice**): Incorporation et diffusion de l'hélium et de l'argon dans l'olivine polycristalline
- 2017 **Léa Florentin** (Université de Lorraine; **examinatrice**): Étude d'inclusions vitreuses dans les olivines des chondres de type I : apport sur la formations de leurs olivines hôtes
- 2017 **Gaëlle Mollex** (Université de Lorraine; **invitée**): Architecture de la plomberie du volcan carbonatitique Oldoinyo Lengai : nouvelles contraintes sur la source, les transferts hydrothermaux, et la différenciation magmatique dans la chambre active
- 2014 **Alice Stephant** (Paris, Muséum national d'histoire naturelle; **examinatrice**): Le rapport isotopique de l'hydrogène dans le système solaire interne : à la recherche des sources physico-chimiques de l'eau planétaire

J'ai aussi été membre de plusieurs comités de suivi de thèses au CRPG (Marion Auxerre, Carolina Cardoso, Valentin Casola et Dorian Thomassin).

2 – Publications

2.1 – Peer-reviewed publications

- [i] Broadley, M.W., D.V. Bekaert, L. Piani, **E. Füre**, B. Marty. Origin of life-forming volatile elements in the inner solar system. *Nature*, *accepted*.
 - [ii] Broadley, M.W., D.J. Byrne, **E. Füre**, L. Zimmermann, B. Marty, R. Okazaki, T. Yada, F. Kitajima, S. Tachibana, K. Yogata, K. Sakamoto, H. Yurimoto, T. Nakamura, T. Noguchi, H. Naraoka, H. Yabuta, S. Watanabe, Y. Tsuda, M. Nishimura, A. Nakato, A. Miyazaki, M. Abe, T. Okada, T. Usui, M. Yoshikawa, T. Saiki, S. Tanaka, F. Terui, S. Nakazawa, and the Hayabusa2-initial-analysis volatile team. The noble gas and nitrogen relationship between Ryugu and carbonaceous chondrites. *GCA*, *under review*
 - [iii] Byrne, D.J., M.W. Broadley, **E. Füre**, L. Tissandier, L. Zimmermann, M.G. Almayrac, D.V. Bekaert, J.A. Barrat, B. Marty. Noble gas and nitrogen investigation of the unique andesitic achondrite Erg Chech 002: Degassing, cosmic ray exposure and radiogenic ingrowth histories. *GCA*, *under review*
 - [iv] Deligny C., **E. Füre**, E. Deloule, A.H. Peslier, F. Faure, Y. Marrocchi. Origin of nitrogen on Mars: First in-situ N isotope analyses of martian meteorites. *GCA*, *under review*
 - [v] Fukuyama, K., K. Hiroyuki, T. Inoue, S. Kakizawa, T. Shinmei, Y. Sano, C. Deligny, **E. Füre**. Temperature and iron content dependence of nitrogen solubility in bridgmanite: evolution of the nitrogen storage of the lower mantle. *EPSL*, *under review*.
 - [vi] Okazaki, R, and the Hayabusa2-initial-analysis volatile team. First asteroid gas sample delivered by the Hayabusa2 mission: A treasure box from Ryugu. *Science Advances*, *under review*
 - [vii] Okazaki, R, and the Hayabusa2-initial-analysis volatile team. Noble gases and nitrogen in samples of asteroid Ryugu record its volatile sources and recent surface evolution. *Science*, *under review*
- [45] Dalou, C., C. Le Losq, **E. Füre**, M.-C. Caumon (2022). Redox controls on H and N speciation and intermolecular isotopic fractionations in aqueous fluids at high pressure and high temperature: Insights from in-situ experiments. *Front. Earth Sci.*, 10:973802. <https://doi.org/10.3389/feart.2022.973802>
 - [44] Condamine, P., S. Tournier, B. Charlier, E. Médard, A. Triantafyllou, C. Dalou, L. Tissandier, D. Lequin, C. Cartier, **E. Füre**, P.G. Burnard, S. Demouchy, Y. Marrocchi (2022). Influence of intensive parameters and assemblies on friction evolution during piston-cylinder experiments. *Am. Mineral.*, 107(8), 1575–1581. <https://doi.org/10.2138/am-2022-7958>
 - [43] Dalou, C., **E. Füre**, C. Deligny (2022). Nitrogen isotope fractionation during magma ocean degassing: tracing the composition of early Earth's atmosphere. *Geochem. Pers. Lett.*, 20, 27–31. <https://doi.org/10.7185/geochemlet.2204>
 - [42] **Füre E.**, L. Zimmermann, H. Hiesinger (2021). Noble gas exposure ages of samples from Cone and North Ray craters: Implications for the recent lunar cratering chronology. *Meteorit. Planet. Sci.*, 56, 2047–2061. <https://doi.org/10.1111/maps.13749>
 - [41] Vernazza, P., P. Beck, O. Ruesch, A. Bischoff, L. Bonal, G. Brennecka, R. Brunetto, H. Busemann, J. Carter, C. Carli, C. Cartier, M. Ciarniello, V. Debaille, A. Delsanti, L. D'Hendecourt, **E. Füre**, O. Groussin, A. Guilbert-Lepoutre, J. Helbert, P. Hoppe, E. Jehin, L. Jorda, A. King, T. Kleine, P. Lamy, J. Lasue, C. Le Guillou, H. Leroux, I. Leya, T. Magna, Y. Marrocchi, A. Morlok, O. Mosis, E. Palomba, L. Piani, E. Quirico, L. Remusat, M. Roskosz, M. Rubin, S. Russell, M. Schönbächler, N. Thomas, J. Villeneuve, V. Vinogradoff, P. Wurz, B. Zanda (2021). Sample return of primitive matter from the outer Solar System. *Experimental Astronomy*. <https://doi.org/10.1007/s10686-021-09811-y>
 - [40] Deligny, C., **E. Füre**, E. Deloule (2021). Origin and timing of volatile delivery (N, H) to the angrite parent body: Constraints from in situ analyses of melt inclusions (2021). *Geochim. Cosmochim. Ac.*, 313, 243–256. <https://doi.org/10.1016/j.gca.2021.07.038>

- [39] **Füre E.**, M. Portnyagin, N. Mironov, N., C. Deligny, A. Gurenko, R. Botcharnikov, F. Holtz. (2021). In situ quantification of the N content of olivine-hosted melt inclusions from Klyuchevskoy Volcano (Kamchatka): Implications for nitrogen recycling at subduction zones. *Chem. Geol.*, 582, 120456. <https://doi.org/10.1016/j.chemgeo.2021.120456>
- [38] Gaillard, F., M.A. Bouhifd, **E. Füre**, V. Malavergne, Y. Marrocchi, L. Noack, G. Ortenzi, M. Roskosz, S. Vulpius (2021). The diverse planetary ingassing/outgassing paths produced over billions of years of magmatic activity. *Space Sci. Rev.*, 217:22. <https://doi.org/10.1007/s11214-021-00802-1>
- [37] Boulliung, J., C. Dalou, L. Tissandier, **E. Füre**, Y. Marrocchi (2021). Nitrogen diffusion in silicate melts under reducing conditions. *Am. Mineral.*, 106, 662–666. <https://doi.org/10.2138/am-2021-7799CCBYNCND>
- [36] Bouden, N., J. Villeneuve, Y. Marrocchi, E. Deloule, **E. Füre**, A. Gurenko, L. Piani, E. Thomassot, P. Peres, F. Fernandes (2021). Triple oxygen isotope measurements by multi-collector secondary ion mass spectrometry. *Front. Earth Sci.*, 8:601169. <https://doi.org/10.3389/feart.2020.601169>
- [35] Bernadou, F., F. Gaillard, **E. Füre**, Y. Marrocchi, A. Slodczyk (2021). Nitrogen solubility in basaltic silicate melt - Implications for degassing processes. *Chem. Geol.*, 573, 120192. <https://doi.org/10.1016/j.chemgeo.2021.120192>
- [34] Bermingham, K.R., **E. Füre**, K. Lodders, B. Marty (2020). The NC-CC isotope dichotomy: Implications for the chemical and isotopic evolution of the early Solar System. *Space Sci. Rev.*, 216:133. <https://doi.org/10.1007/s11214-020-00748-w>
- [33] Füre E., L. Zimmermann, E. Deloule, R. Trappitsch (2020). Cosmic ray effects on the isotope composition of hydrogen and noble gases in lunar samples: Insights from Apollo 12018. *Earth Planet. Sci. Lett.*, 550, 116550. <https://doi.org/10.1016/j.epsl.2020.116550>
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- [31] Curran, N.M., M. Nottingham, L. Alexander, I.A. Crawford, E. Füre, K.H. Joy (2020). A database of noble gases in lunar samples in preparation for mass spectrometry on the Moon. *Planet. Space Sci.*, 182, 104823. <https://doi.org/10.1016/j.pss.2019.104823>
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- [29] Mikhail, S., **E. Füre**. On the origins of Earth's carbon (2019). *Elements*, 15(5), 307–312. <https://doi.org/10.2138/gselements.15.5.307>
- [28] Dalou, C., **E. Füre**, C. Deligny, L. Piani, M.-C. Caumon, M. Laumonier, J. Boulliung, M. Edén (2019). Redox control on nitrogen isotope fractionation during planetary core formation. *PNAS*, 116, 14485–14494. <https://doi.org/10.1073/pnas.1820719116>
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- [26] Mosenfelder J.D., A. von der Handt, **E. Füre**, C. Dalou, R.L. Hervig, G.R. Rossman, M.M. Hirschmann (2019). Nitrogen incorporation in silicates and metals: Results from SIMS, EPMA, FTIR, and laser-extraction mass spectrometry. *Am. Mineral.*, 104, 31–46. <https://doi.org/10.2138/am-2019-6533>
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- [21] Zimmermann, L., G. Avice, P.-H. Blard, B. Marty, **E. Füre**, P. Burnard (2018). A new all-metal induction furnace for noble gas extraction. *Chem. Geol.*, 480, 86–92. <https://doi.org/10.1016/j.chemgeo.2017.09.018>
- [20] **Füre, E.**, E. Deloule, R. Trappitsch (2017). The production rate of cosmogenic deuterium at the Moon's surface. *Earth Planet. Sci. Lett.*, 474, 76–82. <https://doi.org/10.1016/j.epsl.2017.05.042>
- [19] Caracausi, A., G. Avice, P.G. Burnard, **E. Füre**, B. Marty (2016). Chondritic Xenon in the Earth's mantle. *Nature*, 533, 82–85. <https://doi.org/10.1038/nature17434>
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- [17] **Füre, E.**, P.H. Barry, L. Taylor, B. Marty (2015). Indigenous nitrogen in the Moon: Constraints from coupled nitrogen-noble gas analyses of mare basalts. *Earth Planet. Sci. Lett.*, 431, 195–205. <https://doi.org/10.1016/j.epsl.2015.09.022>
- [16] Zimmermann, L., **E. Füre**, P. Burnard (2015). Purification des gaz rares sous ultra-vide – Méthodes de purification. *Techniques de l'ingénieur*, J6635.
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- [14] Bonal L., R. Brunetto R. P. Beck, E. Dartois, Z. Dionnet, Z. Djouadi, J. Duprat, **E. Füre**, Y. Kakazu, P. Oudayer, E. Quirico, C. Engrand (2015). Visible-IR and Raman micro-spectroscopic investigation of three Itokawa particles collected by Hayabusa: mineralogy and degree of space weathering based on non-destructive analyses. *MAPS*, 50(9), 1562–1576. <https://doi.org/10.1111/maps.12496>
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- [12] Fischer, T.P., C. Ramirez, R.A. Mora Amador, D.R. Hilton, J. D. Barnes, Z.D. Sharp, M. Le Brun, J. M. de Moor, P.H. Barry, **E. Füre**, A.M. Shaw (2015). Temporal variations in fumarole gas chemistry at Poás volcano, Costa Rica. *JVGR*, 294, 56–70. <https://doi.org/10.1016/j.jvolgeores.2015.02.002>
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2.2 – Conference presentations (as the presenting author, since 2010)

- Füre, E., M. Portnyagin, N. Mironov, C. Deligny, A. Gurenko, R. Botcharnikov, F. Holtz (2022). Constraints on N recycling at subduction zones from in situ analyses of melt inclusions. *23rd General Meeting of the International Mineralogical Association*, Lyon, FR. **Invited presentation.**
- Füre, E., L. Zimmermann (2021). Use of the 3F4M Noblesse HR at CRPG for N and noble gas analyses. *Nu Instruments webinar.*
- Füre, E., M. Portnyagin, N. Mironov, C. Deligny, A. Gurenko, R. Botcharnikov, F. Holtz (2021). First in situ analyses of nitrogen in primitive subduction-related melts. *Virtual Goldschmidt Conference.* **Invited presentation.**
- Füre, E., L. Zimmermann, H. Hiesinger (2021). The controversial noble gas exposure ages of samples from Cone and North Ray craters: Implications for the recent lunar cratering chronology. *Virtual DINGUE (Developments In Noble Gas Understanding and Expertise) VII workshop.*
- Füre, E. (2020). Origin and distribution of volatile elements in the early Solar System. *Virtual Goldschmidt Conference.* **Keynote presentation.**
- Füre, E., L. Zimmermann, E. Deloule, A.E. Saal (2019). Searching for indigenous noble gases on the Moon. *DINGUE (Developments In Noble Gas Understanding and Expertise) VI workshop*, Zurich, CH.
- Füre, E. (2019). Origin and evolution of terrestrial nitrogen. *Seminar "Origin and evolution of planetary atmospheres - Earth, Mars, Venus"*, Fondation des Treilles, Tourtour, FR.
- Füre, E. (2019). Origin and evolution of volatiles on the Moon. *Workshop "Outgassing processes"*, Villefrance-sur-Mer, FR.
- Füre, E., L. Zimmermann, E. Deloule, A.E. Saal (2019). The H-noble gas signature of single Apollo volcanic glass beads. *50th Lunar and Planetary Science Conference*, Houston, USA.
- Füre, E. (2018). Nitrogen isotope variations in the Solar System (from space missions). *ISSI workshop "Reading terrestrial planet evolution in isotopes and element measurements"*, Bern, CH.
- Füre, E., E. Deloule, R. Trappitsch, A.E. Saal, L. Zimmermann, A. Gurenko, B. Marty (2018). Tracing the source(s) of lunar water. *Journées de bilan et prospective du PNP*, Nice, FR.
- Füre, E. (2018). The origin of Earth's carbon. *Catastrophic perturbations of Earth's carbon cycle workshop*, Reykjavik, IS.
- Füre, E., B. Marty, L. Zimmermann (2018). Origin of volatiles (H, N, noble gases) on the Moon: Constraints from analyses of single lunar soil grains. *CNSA-ESA workshop on Chinese-European cooperation in lunar science*, Amsterdam, NL.
- Füre, E., L. Zimmermann, A.E. Saal (2018). The noble gas bouillabaisse in Apollo 15426 green glasses. *European Lunar Symposium*, Toulouse, FR.

- Füre, E. (2018). Nitrogen isotope variations in the Solar System. *École d'hiver "Origin and evolution of water and associated volatile elements carbon, nitrogen, noble gases in the early Solar System"*, Les Houches, FR.
- Füre, E. (2018). Water and other volatiles in the Moon's interior. *École d'hiver "Origin and evolution of water and associated volatile elements carbon, nitrogen, noble gases in the early Solar System"*, Les Houches, FR.
- Füre, E. (2018). N isotope variations in the Solar System - Open questions. *ISSI workshop "Role of sample return in addressing major outstanding questions in planetary sciences"*, Bern, CH.
- Füre, E., E. Deloule, C. Dalou (2017). Towards new constraints on the origin and budget of terrestrial N. *Goldschmidt Conference*, Paris, FR. Poster presentation.
- Füre, E. (2017). Cosmogenic nuclides in lunar samples. *CNSA-ESA workshop on lunar samples*, Beijing, CN.
- Füre, E., E. Deloule, R. Trappitsch (2017). Reevaluating the source(s) of 'water' in lunar volcanic glasses using a new estimate of the cosmogenic deuterium production rate. *European Lunar Symposium*, Münster, DE.
- Füre, E., E. Deloule, C. Dalou (2017). Searching for "deep" nitrogen through SIMS analyses of undegassed basaltic glasses. *Third DCO International Science Meeting*, St. Andrews, UK.
- Füre, E., E. Deloule, R. Trappitsch (2017). Re-evaluating the source(s) of lunar 'water' using a new estimate of the cosmogenic deuterium production rate. *Workshop on "Accretion, differentiation and early evolution of the terrestrial planets"*, Nice, FR.
- Füre, E. and B. Marty (2016). Nitrogen isotope as tracers of volatile source in the inner Solar System, Yokohama, JP. **Keynote presentation.**
- Füre, E., J.D. Carpenter, I.P. Wright, and the PROSPECT User Group (2016). In-situ volatile (H, C, N, O, noble gases) analyses at the lunar South Pole with ESA's PROSPECT. *DINGUE (Developments In Noble Gas Understanding and Expertise) IV workshop*, Nancy, FR.
- Füre, E., E. Deloule (2016). New constraints on the production rate of cosmogenic deuterium at the Moon's surface. *47th Lunar and Planetary Science Conference*, Houston, The Woodlands, USA.
- Füre, E., P.H. Barry, L.A. Taylor, B. Marty (2015). Origin of nitrogen in lunar basalts. *Goldschmidt Conference*, Prague, CZ.
- Füre, E., P.H. Barry, L.A. Taylor, B. Marty (2015). Nitrogen and noble gases in lunar basalts: Clues to the origin of nitrogen in the Moon's interior. *European Lunar Symposium*, Frascati, IT.
- Füre, E. and B. Marty (2014). Origins and concentrations of volatiles in the interiors of the terrestrial planets, *Goldschmidt Conference*, Sacramento, USA. **Invited presentation.**
- Füre, E., M. Chaussidon, B. Marty (2014) Constraints on the N isotopic evolution of the solar nebula from volatile analyses of a CAI, *Goldschmidt Conference*, Sacramento, USA. Poster presentation.
- Füre, E., B. Marty, E. Deloule, A. Gurenko (2014). Origin of lunar water and nitrogen: Constraints from Apollo 17 volcanic glasses. *European Lunar Symposium*, London, UK. **Keynote presentation.**
- Füre, E., B. Marty, E. Deloule, A. Gurenko (2013) Evidence for chondritic lunar water and nitrogen trapped in Apollo 17 volcanic glasses, *Goldschmidt Conference*, Florence, IT.
- Füre, E., E. Deloule, A. Gurenko, B. Marty (2013) Constraints on the origin of lunar 'water' from D/H and noble gas analyses of single Apollo 17 volcanic glasses. *44th Lunar and Planetary Science Conference*, Houston, USA.
- Füre, E., B. Marty (2012) Helium isotopes in Stardus cometary matter: A possible record of the early evolution of the Solar System. *43rd Lunar and Planetary Science Conference*, Houston, USA. Poster presentation.
- Füre, E., B. Marty, S.S. Assonov (2011) Origin and flux of lunar (micro-)impactors: constraints from N-Ar analyses of single Luna 24 grains. *Goldschmidt Conference*, Prague, CZ.

In addition to the abstracts listed above, I have been included as a co-author on numerous conference abstracts. I have also been invited to present my research as seminar presentations at several universities (e.g., in Milton Keynes, Grenoble, Copenhagen, Bern, Nantes, Oxford, Clermont-Ferrand, St. Andrews, Bayreuth).

3 – Summary of previous research

My doctoral and postdoctoral research projects focused on the use of isotopic signatures of volatiles (noble gases, H, C, N) in various types of terrestrial and extraterrestrial samples – originating from the ocean floor of the Pacific and Indian Ocean to the asteroid belt and beyond – to address a wide range of questions in geo- and cosmochemistry. The objective, analytical approach, and main conclusion of each project are briefly summarized here.

For my **PhD in Earth Sciences at Scripps Institution of Oceanography**, University of California San Diego, under the supervision of Prof. David Hilton, I investigated the origin, transport, and behavior of volatiles (noble gases and CO₂) at four different geological settings – *i*) the San Andreas Fault Zone, a transform plate boundary, *ii*) the Costa Rica margin, a convergent plate boundary, *iii*) Iceland, a ridge-centered hotspot, and *iv*) the Central Indian Ridge, a mid-ocean ridge segment near the off-axis Réunion hotspot. Over the course of several field campaigns and six oceanographic research cruises (including two dives with the submersible DSV *Alvin*), I collected a variety of samples, such as submarine cold seep fluids, fumarolic gases, thermal spring waters, geothermal well gases/fluids, glassy basaltic rocks, as well as olivine-rich volcanic rocks. I then determined the noble gas isotopic composition of the samples by quadrupole or noble gas mass spectrometry and their carbon isotopic ratio by stable isotope mass spectrometry. In addition to my thesis projects, I analyzed gas samples from Oldoinyo Lengai volcano (Tanzania) and from Poás and Turrialba volcanoes (Costa Rica) to better understand the volatile characteristics of the carbonatite mantle source (Fischer et al., 2009) and to trace temporal variations in fumarole gas chemistry (Hilton et al., 2010; Fischer et al., 2015), respectively. Overall, my thesis work resulted in four first-author publications as well as co-authorship of six additional articles.

For the first part of my thesis work (Füre et al., 2009), we chose **cold seep sites at Extrovert Cliff in Monterey Bay** (California, USA) for deployment of submarine flux meters and continuous sampling of fluids over several weeks (**Figure 3.1.**). The aims of this study were to (1) establish the feasibility of the instrumentation in capturing and preserving submarine fluids for subsequent noble gas (He, Ne) and CO₂ analyses and (2) assess if we can produce a near-continuous record of volatile concentrations and isotope variations in a natural system without recourse to conventional high-frequency sampling. In parallel, to obtain noble gas results on small quantities of fluids, we constructed a new dedicated noble gas purification system that was interfaced directly to the preparation line of the MAP 215 noble gas mass spectrometer in SIO's Fluids and Volatiles Laboratory. The new ultra-high-vacuum extraction system led to a decrease of a factor of ~10 in the volume of fluid required for helium isotope analyses at the same analytical precision as obtained previously by 'off-line' noble gas extraction. Our study of submarine cold seep fluids at Extrovert Cliff demonstrated that the Chemical and Aqueous Transport (CAT) meter is capable of capturing and preserving fluids for post-recovery analyses of dissolved volatiles (**Figure 3.1.**), and that it is possible

to produce a near-continuous volatile record over prolonged deployments, up to 18 weeks or more. The helium and neon abundance and isotope characteristics of the sampled cold seep fluids were highly variable on time scales of only a few hours, mainly due to changes in the tidal overburden pressure in the bay and an episodic input of mantle-derived helium. We concluded that the active strike-slip faults and subsidiary cross faults that cut across Monterey Bay subparallel to the main San Andreas Fault trace provide the conduits for mantle fluids to traverse the crust and impart elevated $^3\text{He}/^4\text{He}$ ratios (up to $2.3 R_A$, where $R_A = \text{air } ^3\text{He}/^4\text{He}$) to fluids that are dominated by air-derived helium. The significant variability in helium concentrations, isotopic compositions, and flow rates of the seep fluids demonstrated the necessity for continuous sampling over longer time periods to detect transient earthquake-induced changes in the volatile record at fault zones.

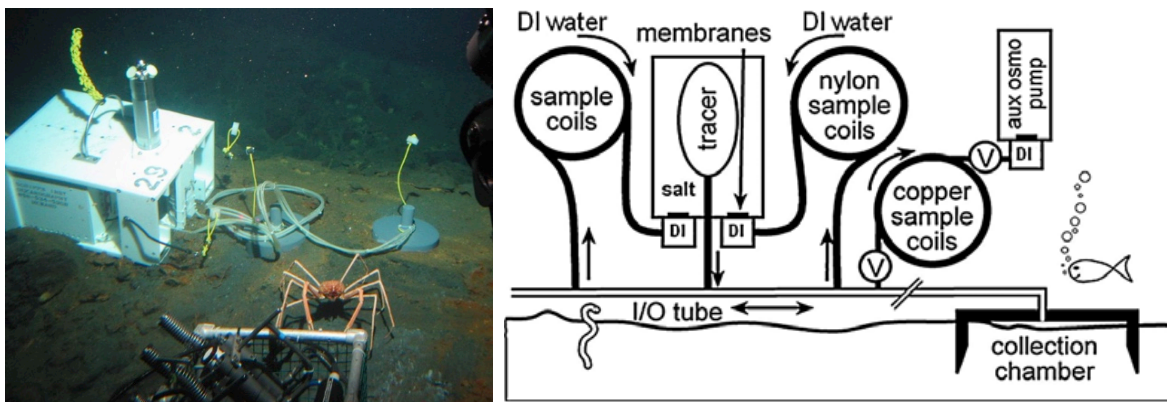


Figure 3.1. Chemical and Aqueous Transport (CAT) meter (Tryon et al., 2001). The CAT meter is designed to measure seep fluid flow at the seafloor by channeling fluids, sampled via a collection chamber placed over the focus of the seep, through the instrument. Over the duration of the deployment, plastic sampling coils preserve a serial record of major ion concentrations and seep fluid flow rates (inferred from the degree of dilution of a chemical tracer), whereas 1/8-inch diameter copper coils capture fluids for subsequent laboratory determination of dissolved volatile (noble gases, CO_2) characteristics.

The goal of my second thesis project was to better constrain the carbon mass balance for the Central America convergent margin, and, hence, to determine the fate of carbon during subduction zone processes. To this end, we investigated the **(He–) CO_2 isotope and abundance systematics of submarine seep fluids emanating at the Costa Rica fore-arc** (Füre et al., 2010a). Seep fluids were sampled at two mud volcanoes (Mound 11 and Mound 12) in copper tubing attached to CAT meters operating in continuous pumping mode. The submarine flux meters were deployed during an oceanographic research cruise in June 2005 using the DSV *Alvin* operated from R/V *Atlantis*. After a period of 12 months, the instruments were retrieved from the seafloor for subsequent laboratory determination of flow rates, major ion concentrations, and dissolved volatile (He, CO_2) characteristics. The quasi-continuous time series records revealed that the carbon emissions and fluid flow rates fluctuated remarkably over the 12-month sampling period. In spite of the spatial and temporal variability, we concluded that the total extrapolated carbon output (CO_2 plus methane) through submarine fluid venting at mound structures at the Costa Rica fore-arc is significantly lower than the

amount of carbon that is potentially available by subducted sedimentary input via the trench (**Figure 3.2.**). This suggested that the loss of slab-derived carbon in the fore-arc region is a negligible part of the carbon mass balance for the Costa Rica subduction zone, and most of the carbon being subducted in Costa Rica must be recycled to the (deeper) mantle, i.e., the zone of arc magma generation and beyond. It is noteworthy that my participation in this project subsequently led me to join the scientific steering committee of the "Reservoirs and Fluxes" community of the Deep Carbon Observatory (DCO); the DCO was a global community of more than 1000 scientists on a ten-year quest to understand the quantities, movements, forms, and origins of carbon in Earth.

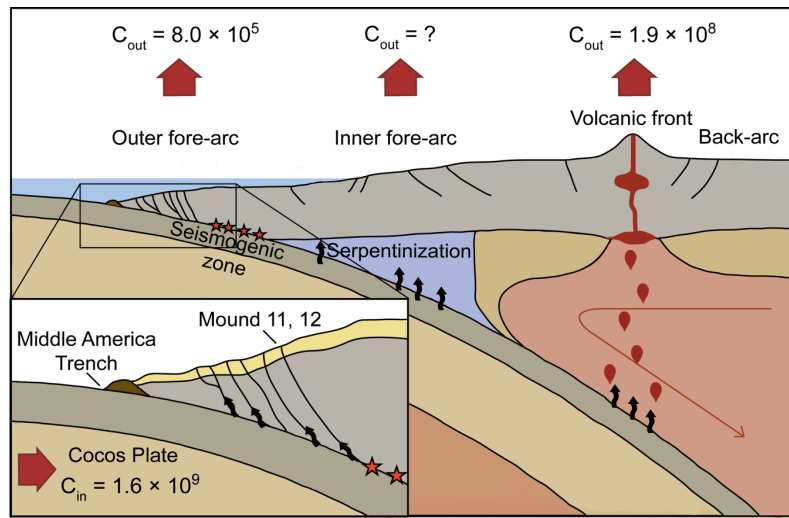


Figure 3.2. Simplified cartoon illustrating the carbon input and output fluxes (in $\text{g C km}^{-1} \text{yr}^{-1}$) at the Central America convergent margin. The inset shows the location of Mound 11 and Mound 12, ~ 30 km arcward from the Middle America trench. The carbon output through submarine fluid venting at the outer fore arc is estimated to be on the order of $8.0 \times 10^5 \text{ g C km}^{-1} \text{yr}^{-1}$, which is virtually negligible compared to the total sedimentary carbon input to the margin and the output at the volcanic front. From Füre et al. (2010a).

My next goal was to examine the **He–Ne systematics of geothermal fluids and the He–Ne–Ar isotope and relative abundance characteristics of subglacial glasses from Iceland** (Füre et al., 2010b). Previous studies of Icelandic basalts found trapped neon with a solar-like isotopic composition accompanied by helium with $^3\text{He}/^4\text{He}$ ratios significantly lower than solar values. However, these studies focused on one segment of Iceland's neovolcanic zones (the Reykjanes Peninsula), whereas the highest $^3\text{He}/^4\text{He}$ ratios (i.e., minimal radiogenic He additions) were found in basalts erupted in Central Iceland and Vestfirðir – the northwest peninsula of Iceland. Therefore, in our study, we collected lavas and geothermal fluids from throughout the Icelandic neovolcanic zones and from older parts of the Icelandic crust to investigate the likely processes contributing to the apparent decoupling of the He and Ne isotope compositions observed previously on the Reykjanes Peninsula (**Figure 3.3.**). Our combined He–Ne(–Ar) study of Icelandic geothermal fluids (from 50 individual localities) and basaltic glasses, olivine, and clinopyroxene phenocrysts (from 89 locations) confirmed that the different segments of the neovolcanic zones in Iceland are characterized by distinct noble gas isotopic signatures. Overall, we concluded that the He–Ne–Ar systematics of Icelandic

subglacial glasses are imprinted with the overlapping effects of He depletion relative to Ne and Ar in the parental melt, binary mixing between a primordial and a MORB-like mantle component, followed by open-system equilibrium degassing, and interaction with air. The same sample suite subsequently allowed us to investigate the processes controlling the CO₂ abundances and isotope variations (Barry et al., 2014) as well as the nitrogen content and isotopic compositions of mantle-derived melts and gases throughout Iceland (Halldórsson et al., 2015).

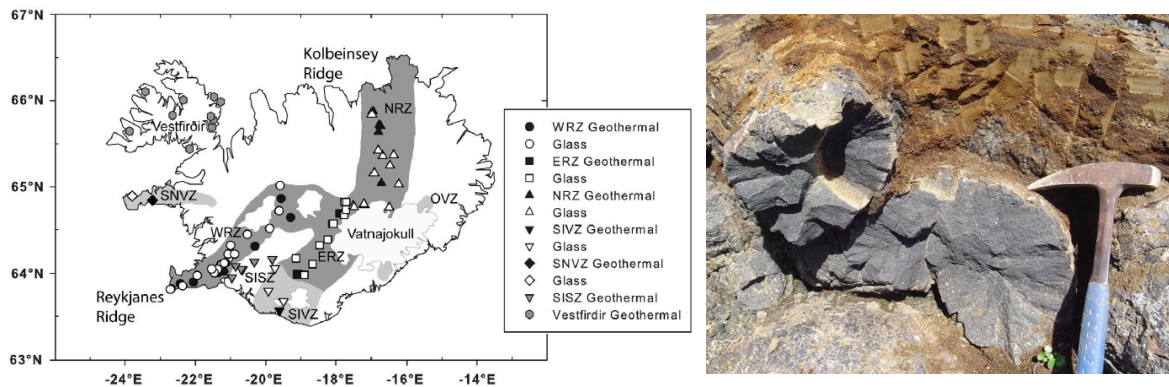


Figure 3.3. Left: Map of Iceland showing the locations of samples that we collected over three sampling campaigns (2006, 2007, 2008; Barry et al. 2014; Füre et al. 2010; Halldórsson et al. 2015). The Western (WRZ), Eastern (ERZ), and Northern rift zones (NRZ) are shaded with dark grey, whereas transitional-alkalic to alkalic off-axis volcanic zones, i.e., the South Iceland Volcanic Zone (SIVZ), Snæfellsnes Volcanic Zone (SNVZ), and Öraefajökull Volcanic Zone (OVZ), are shown in light grey. Also shown are the South Iceland Seismic Zone (SISZ), Vestfirðir (the northwest peninsula of Iceland), and the adjacent submarine Reykjanes and Kolbeinsey ridge segments. Sample locations for geothermal fluids are denoted with closed symbols, and open symbols are used for basalts. Right: Subglacial pillow basalts with glassy rims (Kálfstindar, WRZ.)

Finally, I investigated the postulated **interaction between the Central Indian Ridge (CIR) and the Réunion hotspot**, presently located ~1100 km off-axis to the west (Füre et al., 2011) (Figure 3.4.). The CIR presumably passed over the hotspot ~34 Ma ago, and the aims of this study were to test if CIR basalts still record a Réunion-like helium isotope signature at the present day, and, if this is the case, to understand the dynamics of mixing between different mantle components in this region of the Indian Ocean Basin. During the 19-day KNOX11RR cruise on the R/V *Revelle* (November 2007, Seychelles to Mauritius) – for which I had obtained funding from UC ship funds and acted as chief scientist –, we performed the first extensive helium isotope survey of the CIR axis between 16.7°S and 20.6°S, and the adjacent Gasitao, Three Magi, and Rodrigues ridges to the west of the CIR (Figure 3.4.). Basaltic glasses from 24 dredge locations were supplemented by 26 samples collected during two previous cruises. We also sampled subaerial olivine-phenocryst-rich lavas on the Mascarene Islands (Rodrigues, Mauritius, and Réunion), as well as cumulate xenoliths from Piton Chisny (Réunion Island). We found that helium isotope ratios in submarine basaltic glasses range from 7.1 to 12.2 R_A and lie between values of mid-ocean ridge basalts (MORB; 8 ± 1 R_A) and lavas from Réunion Island (11.5 to 14.1 R_A). The highest ³He/⁴He values (up to 12.2 R_A) were observed in glasses recovered between ~19° and 20°S along the CIR axis and off-axis from the Three Magi and Gasitao

ridges, consistent with lateral flow of hot spot mantle from Réunion toward the CIR, over a distance of ~1100 km. I also note here that our submarine glasses from the CIR were subsequently included in a worldwide sample collection of MORBs to examine the concentration of carbon in primary MORB melts as well as the flux of CO₂ from the global mid-ocean ridge system (Le Voyer et al., 2019).

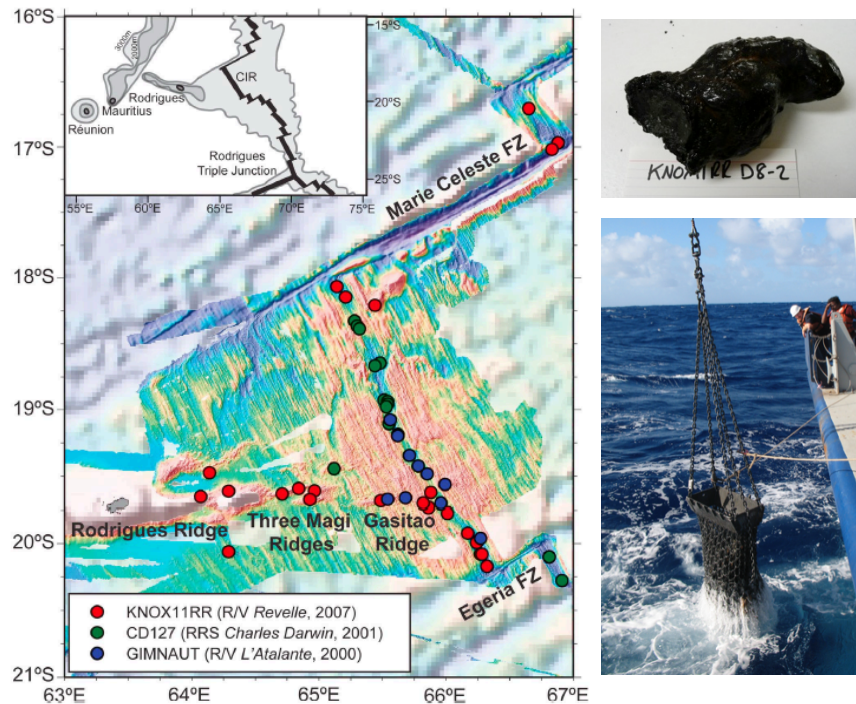


Figure 3.4. Left: Bathymetric map of the CIR and the adjacent Gasitao Ridge, the Three Magi Ridges, and the Rodrigues Ridge. The red circles indicate the locations of samples collected during the multi-national, joint geochemical sampling and geophysical surveying KNOX11RR cruise (Chief scientist: Evelyn Füre). The inset shows the Mascarene Islands (Réunion, Mauritius, and Rodrigues) to the west of the CIR. Right: Submarine pillow basalt fragments (top) were recovered from 24 dredges (bottom) during the KNOX11RR cruise.

As a first step towards improving my understanding of the origin, distribution, and evolution of volatile elements in different solar system objects and reservoirs, I investigated the noble gas (He, Ne) isotopic composition of samples from comet 81P/Wild 2 returned by NASA's *Stardust* mission during my **postdoctoral research at CRPG**, funded by the Centre National d'Etudes Spatiales (CNES). Once my request for samples from the NASA *Stardust* sample collection was approved, I got my first opportunity to analyze extremely small and rare extraterrestrial samples. The spans of helium and neon isotopic compositions in the ***Stardust* aerogel fragments** – analyzed at CRPG and at the University of Minnesota – were found to be extremely broad, implying a similar range for noble gas carriers in the coma of the comet (Palma et al., 2019). In parallel to this analytically challenging and stressful work, I learned to use CO₂ and UV lasers for noble gas extraction from small-sized samples, and I was trained in secondary ion mass spectrometry (SIMS) for *in situ* isotope (H, O, Mg) analyses. By coupling noble gas mass spectrometry with SIMS analyses, I was able to assess the origin of volatiles in other extraterrestrial objects, such as lunar volcanic glasses (LVGs; **Figure 3.5.**) and a Ca–Al-rich inclusion (CAI; **Figure 3.6.**); these studies laid the groundwork for my subsequent research.

To assess the abundance, isotopic composition, and origin of water in the Moon's interior from samples collected at the lunar surface, the contribution of solar wind (SW)-derived hydrogen and of cosmogenic deuterium produced *in situ* needs to be quantified. To determine the proportion of solar, cosmogenic, and indigenous water (hydrogen) trapped in individual Ti-rich LVGs from the 74002 core collected during the *Apollo 17* mission, I coupled SIMS measurements of water abundances and D/H ratios with CO₂ laser extraction–static mass spectrometry analyses of noble gases (He, Ne, Ar) (Füre et al., 2014). The large (~300–400 µm in diameter; **Figure 3.5.**) LVGs were found to contain a small amount of SW-derived volatiles implanted at the grain surfaces, as indicated by the small concentrations of solar helium and neon that represent $\leq 5\%$ of the respective total noble gas abundances. The large proportion of volume-correlated cosmogenic gases reflects an exposure duration of ~28 Ma, on average, of the glasses at the lunar surface. These cosmic ray exposure ages were then used, together with published estimates of the production rate of cosmogenic deuterium (P_D), to correct the measured D/H ratios for the effects of spallation reactions induced by galactic cosmic rays. Although I subsequently revised the P_D value based on new, coupled deuterium–noble gas analyses of lunar olivine grains (see **Chapter 7** for details), these results indicated that the hydrogen isotopic composition of water in the melt source of the 74002 LVGs is similar to that of carbonaceous chondrites.

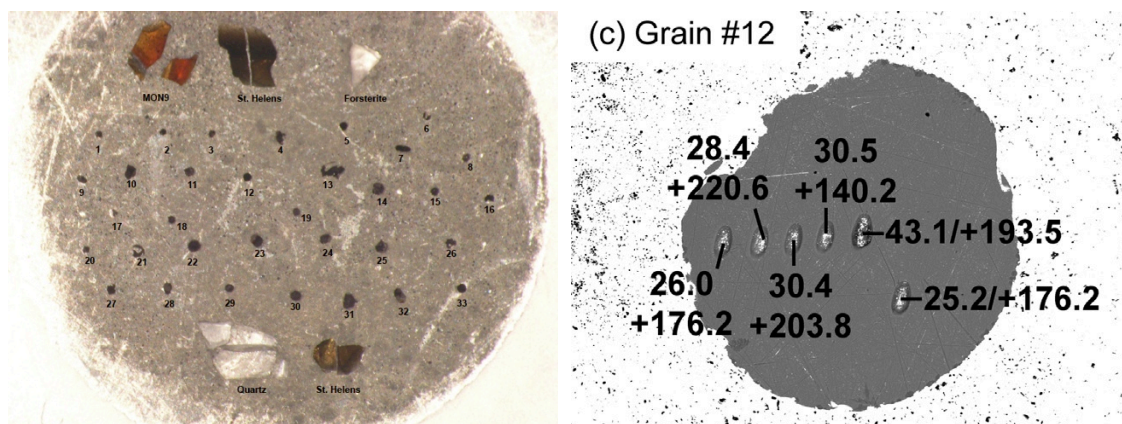


Figure 3.5. Left: Individual ($n = 33$) lunar volcanic glass beads mounted in indium together with four calibrants with known H₂O contents (StHs6/80-G andesitic glass, MON9 pyrope, synthetic forsterite, and a synthetic quartz glass). Right: Backscattered electron image of grain #12. SIMS spots are labeled with the measured water content (ppm) and δD value (‰). From Füre et al. (2014).

To improve our understanding of the spatio-temporal evolution of nitrogen isotope variations in the solar system (see **Chapter 3** for details), I determined the **N and noble gas (Ne–Ar) abundances and isotopic ratios, as well as the Al–Mg and O isotopic compositions, of a large coarse-grained CAI from the CV3 chondrite NWA 816** (Füre et al., 2015a). A section of the CAI was polished and targeted for Mg and O isotope ratio measurements by SIMS, whereas 14 cubes were cut along a profile from the CAI center into the matrix, melted by CO₂ laser heating, and analyzed by static noble gas mass spectrometry (**Figure 3.6.**). We found no evidence of any trapped solar or

planetary noble gases in the CAI; instead, noble gases (Ne and Ar) are purely cosmogenic in origin, i.e., produced *in situ* by the interaction of cosmic rays with elements in the mineral lattice during space exposure of the parent meteorite over a period of ~14 to 20 Ma. The high $(^{26}\text{Al}/^{27}\text{Al})_i$ ratio of $(5.06 \pm 0.50) \times 10^{-5}$ shows that the CAI was last melted 39_{99}^{+109} ka after the “time zero” defined by the bulk CV CAI isochron. The $\delta^{15}\text{N}_{\text{corr}}$ values (i.e., $^{15}\text{N}/^{14}\text{N}$ ratios corrected for the cosmogenic ^{15}N contribution) of $(-15 \pm 9) \text{‰}$ to $(+11 \pm 7) \text{‰}$ imply that the CAI interacted with an isotopically evolved (non-solar) nitrogen reservoir. This either requires an influx of ^{15}N -rich material (e.g., refractory organics) to the inner protoplanetary disk within the first few tens of thousand years of solar system history, or, alternatively, fast radial transport of the CAI into the outer solar system and interaction with a ^{15}N -rich reservoir.

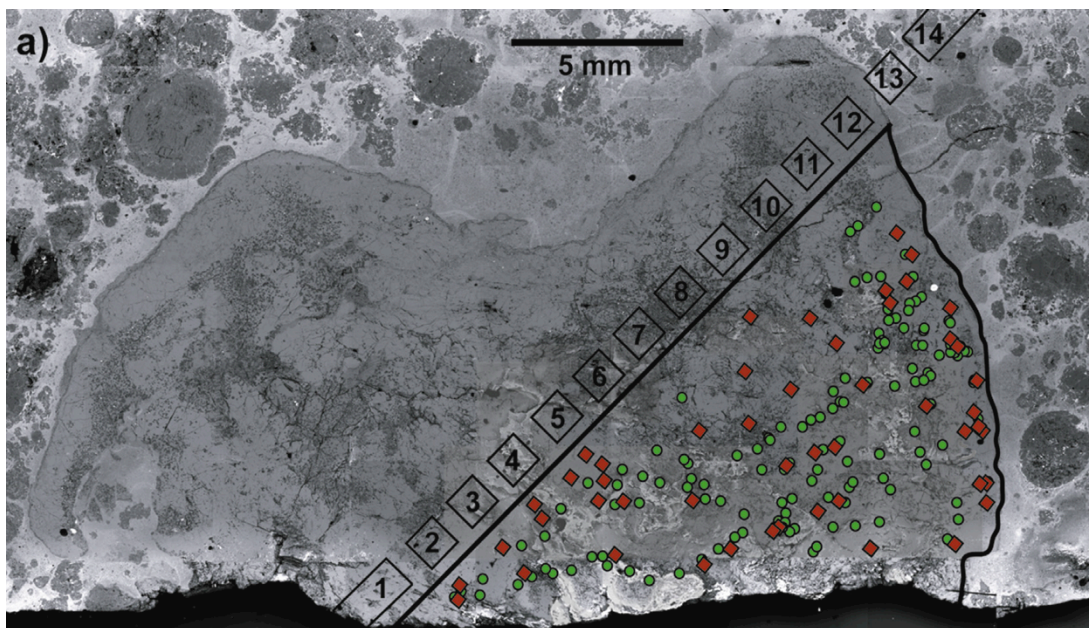


Figure 3.6. Composite backscattered electron image of the NWA 8616 CV3 chondrite sample showing the 14 cubes used for Ne-Ar-N analyses as well as the CAI section selected for SIMS analyses. Red diamonds and green circles indicate the location of the ion probe spots for Al-Mg and O isotope measurements, respectively. From Füre et al. (2015a).

In 2016, I was awarded an **ERC Starting Grant** for my project 'VOLATILIS' (Start date: 1 February 2017, Duration: 66 months). **Since this project has been central to my research over the past 5 years, the scientific background as well as the goals and findings are described in detail in the following chapters.** The key objective of project 'VOLATILIS' was to investigate the origin(s) of volatile elements on Earth and other planetary bodies in the inner solar system. As outlined in **Chapter 4**, given that primitive and differentiated asteroids, planetary embryos, and the Earth-Moon system represent different stages of planet formation in the solar system, N and H isotope measurements of chondritic meteorites, achondrites (e.g., angrites, martian meteorites), the Moon, and Earth can provide constraints on the evolution of planetary volatiles from primordial to present-day compositions. To accurately and precisely determine the isotopic signature of indigenous N trapped in

these various samples, I developed the protocols for N isotope analysis by SIMS and by static mass spectrometry in multi-collection mode; these methods are described in **Chapter 5**. The new SIMS method now allows me to target micron-sized silicate samples (such as melt inclusions in meteorites (**Chapter 6**) and in terrestrial lavas) for *in situ* N analyses, whereas the advances in static mass spectrometry have improved the analytical precision for coupled N–noble gas studies. It should be noted that indigenous volatiles in extraterrestrial samples can be masked by solar and/or cosmogenic contributions; whereas SIMS provides a means to measure N and H away from the outermost sample surface that may contain volatiles implanted by the solar wind, complementary noble gas analyses are key for quantifying cosmogenic ^{15}N and D contributions. Therefore, I have coupled these two high-precision analytical techniques, over the past few years, for several studies of 'water' in lunar samples (**Chapter 7**). In contrast, for our work on angrites and martian meteorites, we have used published cosmic ray exposure (CRE) ages to assess the importance of spallation affects; since access to lab facilities at CRPG was very limited during the COVID-19 crisis, all studied samples could not be analyzed by static noble gas mass spectrometry.

It is important to emphasize that experimental studies provide complementary insights on how various physico-chemical parameters (e.g., oxygen fugacity, pressure, temperature, chemical composition) affect the behavior of volatile elements in fluids, silicate melts, metal alloy melts, and minerals during planetary formation and differentiation. Although this is not the core of my own research, high-pressure and high-temperature experiments (e.g., using internally-heated pressure vessels, piston cylinders, and multi-anvil apparatuses at various institutes, as well as the hydrothermal diamond anvil cell recently installed at CRPG's "Experimental Comochemistry and Magmatology" facility) have allowed me, over the past few years, to investigate *i*) nitrogen solubility and incorporation mechanism(s) in silicate melts (Bernadou et al., 2021; Boulliung et al., 2021, 2020; Mosenfelder et al., 2019) and mantle minerals (e.g., bridgmanite; Fukuyama et al., *under review*), *ii*) nitrogen isotopic fractionation during magma ocean degassing (Dalou et al., 2022), and *iii*) the evolution of the nitrogen isotopic composition of planetary bodies during core formation (Dalou et al., 2019a). The new results obtained through these studies, when combined with data from natural terrestrial and extraterrestrial samples, are fundamental for deciphering the volatile accretion history of planetary bodies in the inner solar system.

4 – Tracing the origin and evolution of volatile elements on planetary bodies in the inner solar system

Knowledge of the origin and inventory of H, C, and N on Earth is fundamental to our understanding of planetary formation processes and the development of habitable conditions. These highly volatile¹ and atmophile ('atmosphere-loving') light elements are abundant in Earth's surface reservoirs (atmosphere and oceans) and play a fundamental role in biogeochemical cycles (e.g., Kaplan, 1975; Rotmans and den Elzen, 1999). However, Earth's interior presumably represents at least an equivalent reservoir for H, C, and N (e.g., Hirschmann, 2018; Marty et al., 2020, 2016; Yoshioka et al., 2018) because they can behave as lithophile ('rock-loving') or siderophile ('metal-loving') elements depending on the pressure (P), temperature (T), oxidation state (oxygen fugacity, fO_2), and silicate and alloy melt compositions prevailing during planetary differentiation (Gaillard et al., 2021). Although our understanding of the behaviors of these elements under magma ocean conditions has improved significantly over the last decades (e.g., Bernadou et al., 2021; Boulling et al., 2020; Dalou et al., 2022, 2019a), their source(s), distribution, and evolution on Earth remain debated in geo- /cosmochemistry, astrophysics, and astrobiology (Albarède, 2009; Bergin et al., 2015; Marty, 2012; Meech and Raymond, 2020; Wu et al., 2018). This stems from the facts that Earth's deep mantle and core are inaccessible and that global geological processes, such as core-mantle differentiation, magma ocean crystallization/degassing, giant impacts, and plate tectonics have modified the primordial volatile abundances and isotopic signatures of terrestrial reservoirs. Consequently, even though potential source(s) of terrestrial volatiles (H, C, N, noble gases) can be retraced by comparing their elemental and isotopic ratios to those of well-characterized cosmochemical endmembers, including the solar nebula, chondritic meteorites², and comets (Alexander, 2017; Hallis et al., 2015; Marty et al., 2016; Péron et al., 2021; Piani et al., 2020), deciphering the volatile accretion history of our planet remains a challenge.

Nitrogen isotopes (^{14}N and ^{15}N) are a powerful volatile source tracer because different solar system objects and reservoirs record distinct $^{15}\text{N}/^{14}\text{N}$ ratios (Füre and Marty, 2015), in spite of efficient mixing and homogenization of matter during solar system formation 4.56 Ga ago. **Figure 4.1.** shows that the solar wind, our best representative of the Sun and the initial composition of the protosolar nebula (PSN), is characterized by very low $^{15}\text{N}/^{14}\text{N}$ ratios³ ($\delta^{15}\text{N} = -383 \pm 8 \text{ ‰}$; Marty et al., 2011). A

¹ Highly volatile elements (H, C, N, O, noble gases) have 50% condensation temperatures below 371 K (for a gas of solar composition at a total pressure of 10^{-4} bar; Lodders, 2003).

² Chondrites are 'primitive' in that their parent bodies did not experience wholesale melting and differentiation. Based on mineralogical, chemical, and isotopic differences, chondrites are divided into carbonaceous, ordinary, and enstatite chondrites. They presumably originate from different parent bodies that accreted at respectively increasing heliocentric distances (e.g., Desch et al., 2018, and references therein).

³ In geochemistry, hydrogen (D/H), carbon ($^{13}\text{C}/^{12}\text{C}$), and nitrogen ($^{15}\text{N}/^{14}\text{N}$) isotopic ratios (here, 'R') are conventionally expressed in delta (δ) notation relative to a standard in units of permil (‰) as: $\delta R = [R_{\text{sample}}/R_{\text{standard}} - 1] \times 1000$. The nitrogen standard is the isotopic ratio of atmospheric N_2 ($^{15}\text{N}/^{14}\text{N}_{\text{air}} = 3.676 \times 10^{-3}$; Nier, 1950). Note that astronomers and astrophysicists generally use the $^{14}\text{N}/^{15}\text{N}$ notation ($^{14}\text{N}/^{15}\text{N}_{\text{air}} = 272$).

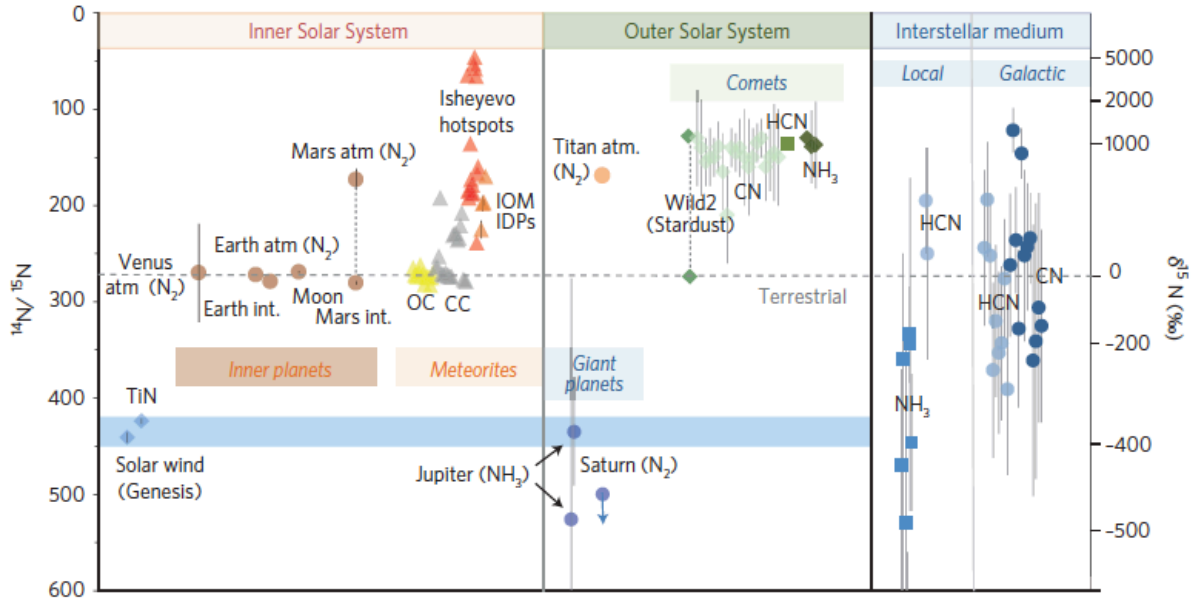


Figure 4.1. Nitrogen isotope variations in solar system objects and reservoirs. The value of the protosolar nebula (PSN; blue shading) is defined by the measurement of SW nitrogen collected by NASA’s Genesis mission (Marty et al., 2011, 2010). Apart from the Sun, TiN (Meibom et al., 2007), and the atmospheres of the giant planets (Fletcher et al., 2014; Fouchet et al., 2000; Owen et al., 2001), all solar system objects and reservoirs are significantly enriched in ^{15}N compared to the PSN. Values determined for various N species in local and galactic molecular clouds (Adande and Ziurys, 2012; Bizzocchi et al., 2010; Dahmen et al., 1995; Gerin et al., 2009; Hily-Blant et al., 2013; Lis et al., 2010) are shown for comparison. Uncertainties of spectroscopic measurements are shown at the 1σ level. Note the nonlinear scale for the right-hand y axis. From Füri and Marty (2015).

similar N isotopic ratio was observed in Jupiter’s atmosphere by spectroscopy and *Galileo* probe mass spectrometer measurements (Fouchet et al., 2000; Owen et al., 2001). Although a comparably low $\delta^{15}\text{N}$ value was also found in a rare N-bearing phase (TiN; osbornite) within a CAI (Meibom et al., 2007), all other solar system objects are enriched in ^{15}N compared to the solar value. Importantly, the isotopic composition of N in Earth’s mantle ($\delta^{15}\text{N} \approx -40$ to -5 ‰ in terrestrial diamonds and mid-ocean ridge basalts) and atmosphere is markedly different from that of the PSN (Cartigny and Marty, 2013; Javoy et al., 1986); this excludes that possibility that terrestrial N was predominantly derived from the dissolution of nebular gas into a magma ocean on the proto-Earth. Potential building blocks of Earth also have non-solar, ^{15}N -enriched isotopic signatures. Most chondrite groups – originating from undifferentiated planetesimals that accreted in the inner and outer solar system⁴ – record ‘bulk’ N isotopic compositions that cluster around the terrestrial value (e.g., Pearson et al., 2006) (Figure 4.1. and 4.2.), but so-called ^{15}N -rich hotspots have been detected at the micrometer scale by ion microprobe analyses in the Isheyevo meteorite (Bonafant et al., 2010; Briani et al., 2009). Hence, by the time the parent bodies of chondrites accreted (i.e., ~ 1.7 – 4.0 Ma after CAIs; Desch et al., 2018; Kruijjer et al., 2020), N in both the inner and outer solar system was predominantly sourced from isotopically

⁴ Non-carbonaceous (NC) and carbonaceous (CC) meteorites record an isotopic dichotomy for neutron-rich isotopes, such as ^{54}Cr (Trinquier et al., 2009) and ^{50}Ti (Leya et al., 2008). This indicates that their parent bodies accreted in two isotopically distinct reservoirs, which were presumably located sunward of (NC) and beyond (CC) the orbit of Jupiter, and remained isolated from each other between ~ 1 and 4 Ma (e.g., Kruijjer et al., 2020, 2017b; Warren, 2011).

processed carriers of non-solar composition (for a recent review, see [Broadley et al., *accepted*](#)). The detection of isotopically heavy N in a CAI, which last interacted with the nebular gas ≤ 0.15 Ma as shown by the ^{26}Al – ^{26}Mg chronometer, suggests that at least some regions of the protoplanetary disk were enriched in ^{15}N within the first few tens of thousand years after solar system formation ([Füri et al., 2015a](#)). Nonetheless, the mechanisms that led to the ^{15}N -enrichment of chondrites and their constituent components (e.g., organic matter) remain a topic of considerable debate and active research (e.g., [Chakraborty et al., 2014](#); [Füri and Marty, 2015](#); [Garani and Lyons, 2020](#); [Heays et al., 2014](#); [Muskatel et al., 2011](#); [Rodgers and Charnley, 2008](#); [Terzieva and Herbst, 2000](#)); self-shielding effects during the photodissociation of nebular N_2 is a viable process to have produced early enrichments in the rarer ^{15}N isotope ([Garani and Lyons, 2021, 2020](#); [Heays et al., 2014](#)), as are specific isotopic exchanges in so-called 'pre-dissociative states' ([Chakraborty et al., 2014](#); [Muskatel et al., 2011](#)) as well as ion–molecule reactions in the cold regions of the disk or pre-solar molecular cloud ([Rodgers and Charnley, 2008](#); [Terzieva and Herbst, 2000](#)). Whereas large ^{15}N excesses are predominantly observed in organic material of chondrites, comets are also characterized by $^{15}\text{N}/^{14}\text{N}$ ratios that correspond to high $\delta^{15}\text{N}$ values of $\sim +1000$ ‰ ([Figure 4.1.](#); [Arpigny et al., 2003](#); [Bockelée-Morvan et al., 2008](#); [Jehin et al., 2009](#); [Rousselot et al., 2014](#); [Shinnaka et al., 2016, 2014](#)). However, it should be noted that cometary $^{15}\text{N}/^{14}\text{N}$ ratios have so far only been determined remotely by radio and optical spectroscopic observations of CN, HCN, and NH_2 (the latter presumably produced by photodissociation of NH_3 ; [Shinnaka et al., 2016](#)), for a limited number of comets from the Oort cloud and Jupiter family, whereas the $^{15}\text{N}/^{14}\text{N}$ value of cometary N_2 is unknown or remains unpublished. The latter species may represent the dominant reservoir of nitrogen in (some) comets ([Rubin et al., 2015](#)), while CN occurs as a trace species ([Owen, 2008](#)). In spite of these limitations, **given the distinct isotopic ratios of solar, chondritic, and cometary N reservoirs, N isotope analyses of pristine samples allow tracing volatile contributions from different solar system sources to Earth and other planetary bodies.** Similar insights into the volatile accretion history of planetary bodies can be

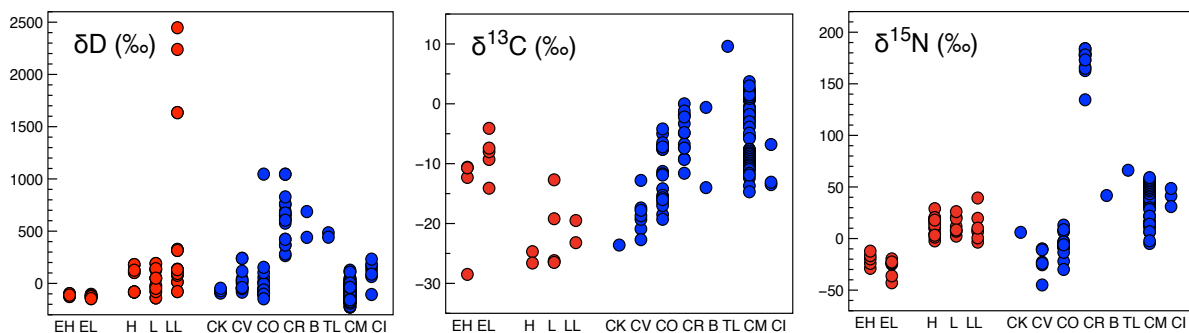


Figure 4.2. H, C, and N isotopic compositions of non-carbonaceous chondrites (NCs), i.e., enstatite (EH, EL) and ordinary (H, L, LL) chondrites, and carbonaceous chondrites (CCs; CK, CV, CO, CR, Bells (B), Tagish Lake (TL), CM, CI). The parent bodies of NC-type meteorites presumably accreted in the inner solar system, whereas those of CC-type meteorites formed beyond Jupiter's orbit. Isotopic ratios (δD , $\delta^{13}\text{C}$, $\delta^{15}\text{N}$) largely overlap between the two reservoirs and between the various chondrite classes and groups. Note the change of vertical scale for the three sub-panels. Modified from [Broadley et al. \(*accepted*\)](#).

Data source: <https://ordar.otelo.univ-lorraine.fr/record?id=10.24396/ORDAR-66>.

gained from H isotope analyses because D/H ratios (δD values) also vary significantly among different solar system objects and reservoirs; compared to the very low D/H ratio of the PSN gas ($\delta D \leq -870$ ‰; Geiss and Gloeckler, 1998), chondrites and comets are enriched in D (Figure 4.2.; Alexander et al., 2012; Alexander, 2017; Piani et al., 2021, 2020), with δD values of up to +2400 ‰ in comet 67P/Churyumov-Gerasimenko (Altwegg et al., 2015). In contrast, the $^{13}\text{C}/^{12}\text{C}$ ratio ($\delta^{13}\text{C}$ value) of the solar photosphere ($\delta^{13}\text{C}_{\text{CO}} = -48 \pm 7$ ‰; Lyons et al., 2018) is only slightly lower than that of 'bulk' chondritic meteorites (Figure 4.2.; Pearson et al., 2006), and cometary $^{13}\text{C}/^{12}\text{C}$ ratios also cluster around the chondritic or terrestrial values (Woods and Willacy, 2009); these observations indicate that carbon isotopes alone cannot be used to discriminate between different volatile sources (Mikhail and Füri, 2019).

Chondritic and differentiated asteroids, Mars, and the Earth-Moon system provide different snapshots of the history of planet formation in the inner solar system, and, as such, these bodies may preserve a record of the evolution of planetary volatiles from primordial to present-day compositions. The material that formed the planets in the inner solar system started out as small dust grains that coagulated to form planetesimals and large planetary embryos, which then accumulated into the terrestrial planets through collisions (Figure 4.3.; for a recent review, see Broadley et al., *accepted*). Given that chondrites originate from undifferentiated planetesimals that were limitedly processed since their original formation at the dawn of the solar system, they represent the least altered materials

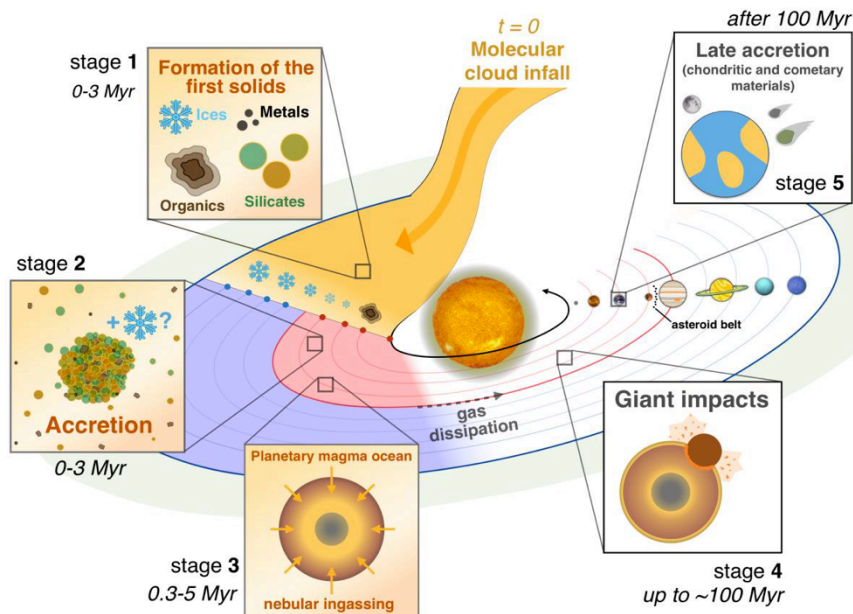


Figure 4.3. Main stages of planet formation and volatile incorporation into terrestrial building blocks. **Stage 1:** Formation of the first solids via condensation of silicates and ices, and polymerization of organic materials. **Stage 2:** Early accretion of the first planetary objects by accumulation of variable amounts of silicates, organics, and ice. **Stage 3:** Planetary bodies that reach a sufficient size to capture nebular atmospheres may experience episodes of nebular ingassing during periods of magma oceans. **Stage 4:** After dissipation of the protosolar nebula gas, planetary embryos may collide during giant impacts, such as the one that formed the Moon. **Stage 5:** After Moon formation, Earth experienced late episodes of chondritic material accretion (generally referred to as the late veneer), accompanied by minor contributions from comets. From Broadley et al. (*accepted*).

from the early protoplanetary disk that can be studied. However, calculated Hf–W model ages of 'magmatic' iron meteorites (combined with thermal modeling of bodies internally heated by ^{26}Al decay) indicate that differentiated planetesimals accreted with the first ~ 1 Ma of solar system history (Spitzer et al., 2021), prior to the formation of the parent bodies of chondrites that are represented in our global meteorite collection (e.g., Desch et al., 2018; Kruijer et al., 2020, and references therein). Based on ^{26}Al – ^{26}Mg and ^{182}Hf – ^{182}W data, the parent body of angrites – a small group of mafic to ultramafic achondrites – is also inferred to have accreted within the first ~ 0.4 to 1.5 Ma after CAI formation (Kleine et al., 2012; Schiller et al., 2015). Mars presumably accreted only slightly later; ^{182}Hf – ^{182}W and ^{60}Fe – ^{60}Ni data suggest that Mars reached half of its size in ~ 1.8 Ma only (Dauphas and Pourmand, 2011; Tang and Dauphas, 2014) and that core formation and magma ocean crystallization were completed ~ 20 – 25 Ma after CAI formation (Bouvier et al., 2018; Kruijer et al., 2017a; Nimmo and Kleine, 2007). Due to its small size and its rapid accretion, Mars is considered to be a stranded planetary embryo (Dauphas and Pourmand, 2011). Hence, the angrite parent body (APB) and Mars may represent analogues of what Earth was like in its initial stages of accretion, and meteorites originating from these bodies are of great interest for investigating the history of volatile incorporation during the earliest stages of planet formation in the inner solar system. The Moon, on the other hand, formed from the debris of a collision between a planetesimal with the differentiated proto-Earth (Cameron, 1997; Hartmann and Davis, 1975). Although the timing of this giant impact remains highly debated (for a recent review, see Lock et al., 2020), the Moon represents the "Rosetta Stone of the solar system" (Urey, 1952), and the lunar regolith provides a key archive of the past 4.5 billion years of the history and evolution of the inner solar system. In summary, **N (and H) isotope analyses of chondrites, iron meteorites, angrites, martian meteorites, and samples returned from the Moon can provide constraints on the origin of Earth's primordial volatiles, and help to assess the importance of volatile storage during primary accretion and differentiation versus late accretion of chondritic and cometary materials towards the end stages of planet formation.**

Understanding the timing of N delivery to planetary bodies in the inner solar system is important. If N was delivered to the terrestrial planets during the main stages of accretion, then early differentiation processes such as magma ocean degassing/crystallization and core formation, for example, likely controlled its elemental and isotopic distribution in Earth's reservoirs. Whereas, over the past decade, numerous experimental studies at variable pressures and temperatures have investigated N speciation (Dalou et al., 2019b; Grewal et al., 2020; Li and Keppler, 2014; Mosenfelder et al., 2019) and solubility in silicate melts (Bernadou et al., 2021; Boulliung et al., 2020; Kadik et al., 2017; Keppler et al., 2022; Libourel et al., 2003; Miyazaki et al., 2004), N solubility in mantle minerals (Li et al., 2013; Yoshioka et al., 2018; Fukuyama et al., 2020; Fukuyama et al., *under review*), as well as N partitioning during metal-silicate segregation (analogous to planetary core formation; Dalou et al., 2017; Grewal et al., 2019; Kadik et al., 2013, 2011; Roskosz et al., 2013;

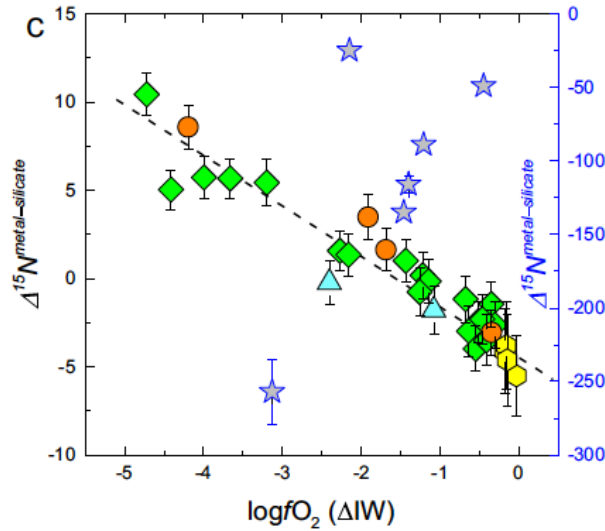


Figure 4.4. The metal-silicate N-isotopic fractionation factor $\Delta^{15}\text{N}^{\text{metal-silicate}}$ as a function of oxygen fugacity ($\log f\text{O}_2$ relative to the iron-wüstite buffer, IW). The $\Delta^{15}\text{N}^{\text{metal-silicate}}$ values from Li et al. (2016) (yellow symbols) and Shi et al. (2022) (green, orange, and blue symbols), determined by static mass spectrometry analyses of silicate glass and metal fragments, appear consistent. In contrast, Dalou et al. (2019a) observed substantial N-isotopic fractionations between metal alloys and silicate melts, i.e., from -257 to -49 ‰ over 3 log units of $f\text{O}_2$ (blue stars and right-hand blue Y axis); these results were obtained by secondary ion mass spectrometry analyses of ^{15}N -spiked samples synthesized in graphite capsules.

Speilmanns et al., 2019, 2018), **the effect of planetary differentiation on the N isotopic composition of Earth's silicate mantle remains poorly understood.** Although the elemental N partitioning between metal alloy and silicate melts is well known, the degree of N isotopic fractionation during planetary core formation is still particularly debated. Li et al. (2016) and Dalou et al. (2019a) both argued that ^{14}N is preferentially incorporated into the metal alloy phase during its segregation, with a metal-silicate N-isotopic fractionation factor ($\Delta^{15}\text{N}^{\text{metal-silicate}}$) that decreases significantly with decreasing oxygen fugacity (**Figure 4.4.**). However, Li et al. (2016) only covered a small range of oxygen fugacities (IW -1.2 to IW -0.66)⁵ in their experiments, and the data from Dalou et al. (2019a) suffered from significant N loss (up to 75%) through the graphite capsule walls, potentially overestimating the degree of N isotopic fractionation between metal alloy and silicate melts at reducing conditions due to a kinetic effect. Recently, Shi et al. (2022) found that metal-silicate N-isotopic fractionation *increases* with decreasing oxygen fugacity (**Figure 4.4.**), in striking contrast to the results from Dalou et al. (2019a). These contrasting findings have fundamentally different implications for the origin and isotopic evolution of N in Earth's mantle, as they suggest that enstatite chondrite-like material ($\delta^{15}\text{N}_{\text{EC}} = -47$ to -13 ‰; **Figure 4.2.**) either may (Dalou et al., 2019a; Li et al., 2016) or may not (Shi et al., 2022) represent the main source of terrestrial N. Therefore, to decipher the N accretion history of our planet, new investigations of the magnitude of N isotopic fractionation between metal alloy and silicate melts, at physico-chemical conditions relevant to planetary core formation and with minimal N loss, are needed. Importantly, since the geochemical behavior of N is

⁵ IW: oxygen fugacity, $f\text{O}_2$, reported in log units relative to the iron-wüstite buffer.

predominantly controlled by the oxygen fugacity, evolution of the redox conditions of Earth's mantle must be taken into account when assessing the importance of N isotopic fractionation during planetary processes. Furthermore, given the complex speciation behavior of N, various species such as molecular N_2 or NH_3 , NH_4^+ , NH_2^- , NH_2^+ , NH^{2-} , CN^- , nitrosyl complexes (e.g., $X-N-O$ or $X-N=O$, where X represents a metal cation), and $X-N^{3-}$ (i.e., nitride complexes) must be considered in the context of a multi-component system when investigating the N solubility and partitioning behavior among minerals, melts, and fluids (e.g., Mosenfelder et al., 2019; Mysen, 2019).

In summary, given that solar, chondritic, and cometary nitrogen (and hydrogen) reservoirs have distinct isotopic signatures, the **origin** of volatiles incorporated into planetesimals and planets can be traced based on N (and H) isotope analyses of mantle-derived samples. Furthermore, the **chronology** of volatile accretion by planetary bodies in the inner solar system can be assessed by targeting chondrites and iron meteorites as well as sample from the APB, Mars, and the Moon. Combined 'bulk' analyses of N and noble gases by **static noble gas mass spectrometry** allow the volatile content of extraterrestrial samples to be resolved into constituent components, i.e., solar, cosmogenic, and indigenous. This approach also permits to determine the cosmic ray exposure (CRE) age (i.e., the total duration of irradiation by cosmic rays) of meteorites or samples returned by space missions which, in turn, is key for correcting measured $^{15}N/^{14}N$ (and D/H) ratios for the contribution of cosmogenic nuclides such as ^{15}N (and D). In contrast, *in situ* analyses of N (and H) by **secondary ion mass spectrometry (SIMS)** allow assessing the spatial distribution of volatiles in different host phases. SIMS is also the key tool for targeting melt inclusions for volatile analyses; these (glassy) inclusions, which are small pockets of silicate melt entrapped during crystal growth, provide the best insights into pre-eruptive concentrations and isotopic ratios of N (and other volatiles) in the parent melt of igneous samples (e.g., Hauri et al., 2011; Saal et al., 2013; Wallace, 2005). Experimental studies provide complementary but fundamental insights on how **planetary differentiation processes** at various physico-chemical conditions (oxygen fugacity, pressure, temperature, chemical composition) may have modified the initial isotopic signature of N accreted by Earth and other planetary bodies. Ultimately, understanding the origin and accretion history of N (and H) on planetary bodies is key for evaluating the astrobiological importance of primitive and differentiated planetesimals and of comets in delivering volatiles and pre-biotic organic materials to the terrestrial planets, and for assessing the origin of life-enabling chemistry.

5 – Analytical development

5.1 – N analysis by static mass spectrometry in multi-collection mode

For geochemical applications, the isotopic composition of nitrogen (N_2) has historically been analyzed using isotope ratio mass spectrometers operated in dynamic pumping mode (e.g., Boyd et al., 1995; Javoy and Pineau, 1991). Since this technique is not suitable for the analysis of small nitrogen abundances, higher-sensitivity noble gas mass spectrometers operated under static vacuum conditions are now the standard method for determining the nitrogen isotopic composition of N-poor and/or small-sized (≤ 5 mg) terrestrial and extraterrestrial samples (Barry et al., 2012; Frick and Pepin, 1981; Hashizume and Marty, 2004; Wright et al., 1988). For this method, nitrogen is extracted from solid samples by using a destructive technique (e.g., crushing, laser ablation, laser- or furnace-heating) and purified following a specific protocol (Humbert et al., 2000; Zimmermann and Marty, 2014). At CRPG's noble gas facility, a VG5400 (Micromass©) noble gas mass spectrometer was in use between 1992 and 2018 for nitrogen and noble gas analyses. The VG5400 operated in mono-collection mode, i.e., nitrogen ion signals were determined sequentially at masses 28 ($^{14}N^{14}N^+$), 29 ($^{15}N^{14}N^+$), and 30 ($^{15}N^{15}N^+$) on a Faraday cup ($R = 10^{11} \Omega$) or an electron multiplier, with the limitation that interfering species (hydrocarbons (C_2H_x), N_2H , CO) could not be (fully) resolved from the peaks of interest (Hashizume and Marty, 2004). Notably, the N_2H^+ signal could be reduced by optimizing the source settings (i.e., by using a low trap current), whereas any residual CO^+ contribution could be corrected for numerically. Following a severe contamination of the nitrogen purification line and mass spectrometer by hydrocarbons (from an unknown source) in 2015, the VG5400 could no longer be used for nitrogen isotope analyses in spite of our efforts to reduce the hydrocarbon signal; the attempted (time-consuming) measures included *i*) baking out the purification line and mass spectrometer, *ii*) taking apart and cleaning the source, *iii*) replacing the filament, *iv*) replacing the electron multiplier, and *v*) replacing the quartz finger containing CuO powder/sticks. Since additional issues with the source and collector electronics as well as with the DOS operating system adversely affected the noble gas analyses, the VG5400 was replaced in July 2018 by a Noblesse HR (Nu Instruments) noble gas mass spectrometer (**Figure 5.1.1.**).

The Noblesse HR is specifically designed for the analysis of noble gases (He, Ne, Ar, Kr, Xe) under static vacuum conditions (e.g., Coble et al., 2011; Péron et al., 2021; Ruzié et al., 2012; Saxton, 2020). It features a single focusing, 75° magnetic sector and a Nier-type ion source. The collectors are fixed and the ion dispersion is adjusted using a patented zoom optics system; this permits various sets of noble gas isotopes to be measured using multi-collection. The two helium isotopes can only be analyzed in peak jumping mode. The instrument installed at CRPG is equipped with three Faraday collectors and four discrete dynode secondary electron multipliers operated in ion-counting (IC) mode in a fixed collector array (3F4M) (**Figure 5.1.1.**). Thus, N_2 abundances and isotopic ratios can be determined by simultaneously measuring ion signals at mass 28 ($^{14}N^{14}N^+$) on Fa2 with a $10^{11} \Omega$

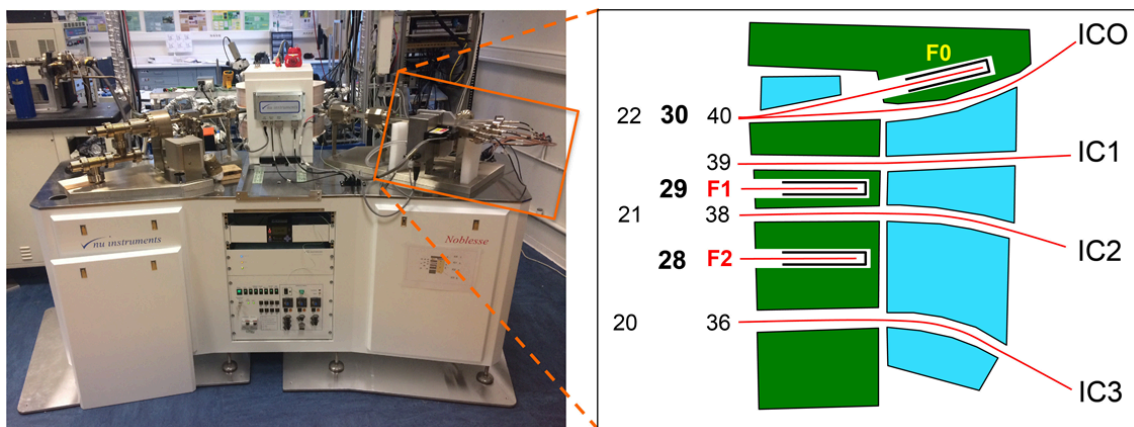


Figure 5.1.1. Left: The 3F4M Noblesse HR noble gas mass spectrometer at CRPG. Right: The collector array includes three Faraday (F) and four electron multiplier (IC) detectors. The three isotopes of neon ($^{20,21,22}\text{Ne}$) and argon ($^{36,38,40}\text{Ar}$) as well as the three nitrogen isotopologues ($^{28,29,30}\text{N}_2$) can be analyzed in multi-collection mode.

amplifier, mass 29 ($^{15}\text{N}^{14}\text{N}^+$) on Fa1 with a $10^{12} \Omega$ amplifier, and mass 30 ($^{15}\text{N}^{15}\text{N}^+$) on IC0. Thanks to the high mass resolution (> 700)⁶ and mass resolving power (> 5000)⁷, interfering peaks are partially separated from those of N_2 . The new analytical procedure, which we developed, consists of first automatically finding the $^{14}\text{N}^{14}\text{N}^+$ peak center at the start of each analysis, and then to measure the collector baselines (Zero), the $^{12}\text{C}^{16}\text{O}^+$ signal (Step 1), the side of the $^{14}\text{N}^{14}\text{N}^+$ peak at $\sim 50\%$ peak height (Step 2), the $^{14}\text{N}^{14}\text{N}^+ + ^{12}\text{C}^{16}\text{O}^+$ signal (together with $^{15}\text{N}^{14}\text{N}^+ + ^{13}\text{C}^{16}\text{O}^+$ and $^{15}\text{N}^{15}\text{N}^+ + ^{12}\text{C}^{18}\text{O}^+$) (Step 3), and the $^{15}\text{N}^{14}\text{N}^+ + ^{14}\text{N}^{14}\text{NH}^+$ and $^{15}\text{N}^{15}\text{N}^+ + ^{15}\text{N}^{14}\text{NH}^+$ signals⁺ (Step 4) (**Figure 5.1.2**). During the entire sequence, the magnet remains fixed, while the ion beam is moved electrostatically using the quad lenses (i.e., using 'Lin2' as a deflector). Following data acquisition (25 measurement cycles), the signals of interest (extrapolated to $t = 0$) are obtained by correcting for the CO contribution.

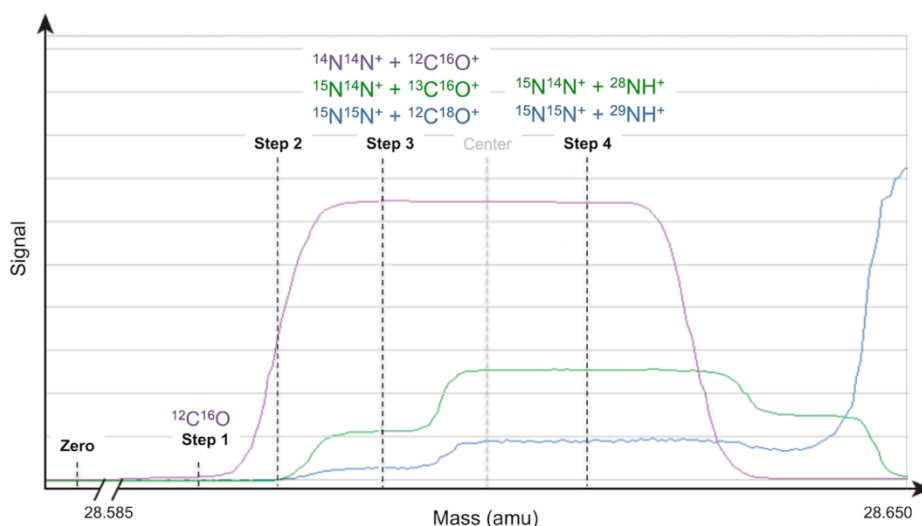


Figure 5.1.2. $^{14}\text{N}^{14}\text{N}^+$ (Fa2, purple), $^{15}\text{N}^{14}\text{N}^+$ (Fa1, green), and $^{15}\text{N}^{15}\text{N}^+$ (IC0, blue) peaks with full-scale peak intensities of 5.0 V, 0.2 V, and 2×10^5 cps, respectively, for a typical air standard. Contributions from $^{14}\text{N}^{14}\text{NH}^+$ and $^{15}\text{N}^{14}\text{NH}^+$ are generally negligible at the start of the analysis but increase during the 25-cycle measurement.

⁶ Mass resolution is a measure of the ability to separate two peaks from one another. $\text{MR} = m/\Delta m$, where Δm corresponds to the peak width at 10 % peak height.

⁷ Mass resolving power is a measure of the steepness of a peak flank. $\text{MRP} = m/\Delta m$, where Δm corresponds to 5 to 95 % on the side of the peak (i.e., the width of the side-of-peak).

By applying this procedure, the reproducibility of repeated N_2 abundance measurements of purified air standards is $\sim 3\%$ (1σ), and N isotopic ratios (i.e., $\delta^{15}N$ values) can be determined with an uncertainty of $\sim 0.5\%$ (**Figure 5.1.3**). Thus, the new technique improves the analytical precision for both N abundance and isotope ratio measurements compared to the results previously obtained by peak-jumping using the VG5400.

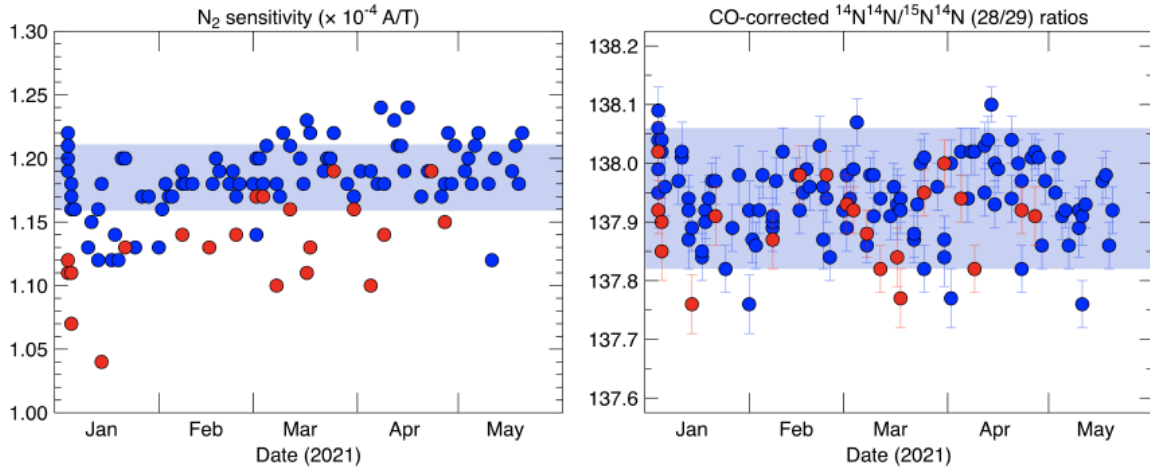


Figure 5.1.3. N_2 ($^{14}N^{14}N^+$) sensitivity (left panel) and CO-corrected $^{14}N^{14}N/^{15}N^{14}N$ ratios (right panel) of unpurified ($n = 91$; blue) and purified ($n = 21$; red) air standards analyzed over a 5-months period in 2021 (at a trap current of $150\ \mu A$).

I carried out the analytical development in close collaboration with Laurent Zimmermann at CRPG's noble gas facility. In addition to developing the protocol for N isotope analyses, we also set up the protocols for noble gas (He, Ne, Ar) isotope analyses by using specific source settings (i.e., extraction voltage, ion repeller voltage). We are currently completing an article discussing the system's configuration and performance for nitrogen and noble gas isotope measurements using multi-collection (Zimmermann et al., *in prep.*), and we were invited to present our work in 2021 as part of the webinar organized by Nu Instruments. Importantly, we used the new methods to precisely determine the nitrogen–noble gas isotopic composition of gas and solid samples that were returned from the asteroid Ryugu by the **Hayabusa2** spacecraft (JAXA) in Dec 2020 (Okazaki et al., *Science Advances*, *under review*; Okazaki et al., *Science*, *under review*).

5.2 – N analysis of silicate glasses by secondary ion mass spectrometry (SIMS)

SIMS N analyses are challenging because N does not form a stable negative ion (N^-), and the useful ion yield of N^+ is relatively low (Mosenfelder et al., 2019). Given that in the presence of C, an intense CN^- signal forms when the sample surface is bombarded with a Cs^+ ion beam (Zinner et al., 1989), most SIMS analyses of N abundances rely on measurement of CN^-/C^- , and N isotopic ratios are routinely determined as $^{12}C^{15}N^-/^{12}C^{14}N^-$ in various C-bearing materials for a wide range of applications in geo- and cosmochemistry (e.g., Aléon et al., 2003a; Busemann et al., 2006; Hauri et al., 2002; Marty et al., 2011; Meibom et al., 2007; Sugiura, 1998a; Thomen et al., 2014; Zinner et al.,

1989). In C-poor or C-free silicate minerals and glasses, the NO^- signal can be targeted for N abundance analyses, as demonstrated by Li et al. (2013) and Regier et al. (2016). The lack of an appropriate analytical protocol, as well as of suitable N-bearing standards, had long prevented the use of SIMS for routine nitrogen isotope analyses of silicates.

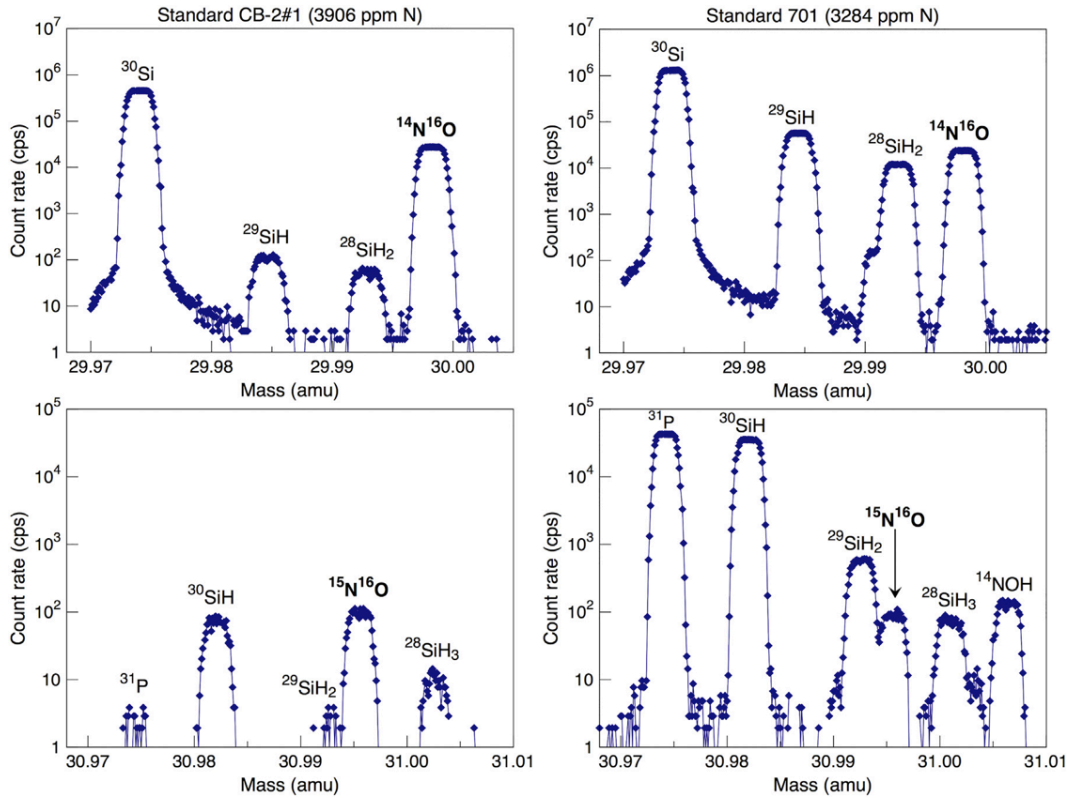


Figure 5.2.1. High-resolution mass spectra at mass stations 30 and 31 for glasses CB-2#1 (left) and 701 (right) obtained with a mass resolution ($m/\Delta m$) of $\sim 11,000$ using the CAMECA IMS 1280 HR at CRPG. Sample CB-2#1 was synthesized at atmospheric pressure in a GERO HTVR 70–250 vertical drop-quench furnace and contains 3906 ± 188 ppm N, whereas sample 701 was synthesized at 1.2 ± 0.1 GPa in a piston cylinder and contains 3284 ± 233 ppm N. CB-2#1 is 'dry', whereas 701 contains 0.8 wt% H_2O . From Füre et al. (2018).

As part of my ERC project 'VOLATILIS', I developed a new protocol for determining precise and accurate N abundances (and $^{15}\text{N}/^{14}\text{N}$ ratios) in silicate glasses by large geometry SIMS (CAMECA IMS 1280 HR) (Füre et al., 2018a). I carried out the analytical development in close collaboration with Etienne Deloule at CRPG's ion probe facility. Twelve (C-)N-bearing synthetic basaltic glasses form our suite of reference materials, supplemented by N-bearing glasses synthesized by Julien Boulliung during his PhD (Boulliung et al., 2020). We found that N abundances in C-free glasses can be measured by targeting the NO^- , AlN^- or SiN^- secondary molecular ions. However, because interferences from various species with $^{27}\text{Al}^{15}\text{N}^-$ and $^{28}\text{Si}^{15}\text{N}^-$ cannot be resolved, N isotopic ratios can only be determined in the form of $^{15}\text{N}^{16}\text{O}^-/^{14}\text{N}^{16}\text{O}^-$ (Figure 5.2.1.). Therefore, N abundances and isotopic ratios in silicate glasses are best investigated by targeting the NO^- signals at mass stations 30 and 31. This method yields N concentrations in silicate glasses of variable composition in excellent agreement with 'bulk' noble gas mass spectrometry analyses, for a wide range of N contents between

≤ 1 and ~ 6000 ppm (**Figure 5.2.2. Boulliung et al., 2020**). N isotopic ratios can be determined with an uncertainty that is small enough to resolve $^{15}\text{N}/^{14}\text{N}$ variations in extraterrestrial silicates or in N-rich synthetic samples. N isotopic ratios of terrestrial samples (e.g., olivine-hosted melt inclusions), however, cannot be determined by this method because their N content is too low (i.e., the $^{15}\text{N}^{16}\text{O}^-$ count rate is near or below the detection limit; e.g., Füre et al., 2021a). It is noteworthy that this method requires a high mass resolution ($m/\Delta m$) of $\geq 11'000$ to separate the $^{15}\text{N}^{16}\text{O}^-$ peak from the neighboring $^{29}\text{SiH}_2^-$ peak at mass 31 (**Figure 5.2.1.**, bottom panels); this is particularly important for water-rich samples such as those synthesized at high pressures. We also found that the presence of phosphates increases the $^{31}\text{P}^-$ peak intensity, which can result in elevated measured $^{15}\text{N}^{16}\text{O}^-/^{14}\text{N}^{16}\text{O}^-$ ratios due to the contribution of the $^{31}\text{P}^-$ peak tail at the mass of $^{15}\text{N}^{16}\text{O}^-$ (Deligny et al., 2021).

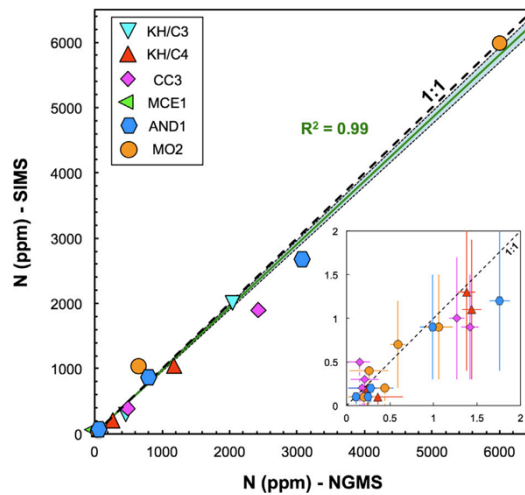


Figure 5.2.2. Comparison of N abundances measured by *in-situ* SIMS and by bulk noble gas mass spectrometry (NGMS) for synthetic glasses of variable compositions. The black dashed line represents the 1:1 correlation, whereas the green line represents the best-fit linear regression with 2σ uncertainties shown in light blue. Low concentration data (< 2 ppm N) are shown on an enlarged scale in the inset. From Boulliung et al. (2020).

The development of this new technique represented the cornerstone of my ERC project 'VOLATILIS'. The advantages and limits of the method were discussed in our article published in *Chemical Geology* in 2018. Since then, I have applied this method for the analysis of various terrestrial, extraterrestrial, and synthetic samples to investigate:

- N isotope fractionation during planetary core formation (Dalou et al., *PNAS*, 2019)
- N solubility in silicate melts of variable compositions (Boulliung et al., *GCA*, 2020)
- N diffusion in silicate melts under reducing conditions (Boulliung et al., *Am. Mineral.*, 2021)
- N solubility in basaltic silicate melts at variable pressures (Bernadou et al., *Chem. Geol.*, 2021)
- N concentrations in olivine-hosted melt inclusions from Kamchatka (Füre et al., *Chem. Geol.*, 2021)
- N concentrations and isotope ratios in melt inclusions in angrites (Deligny et al., *GCA*, 2021)
- N isotope fractionation during magma ocean degassing (Dalou et al., *GPL*, 2022)
- N solubility in bridgmanite (Fukuyama et al., *under review*)
- N concentrations and isotope ratios in melt inclusions in martian meteorites (Deligny et al., *under review*)

The results obtained for melt inclusions in angrites and martian meteorites are discussed in detail in the following chapter.

It is noteworthy that for all previous N analyses of silicates (glasses, minerals) by SIMS at CRPG, we used synthetic glasses as calibrants. To better assess possible matrix effects on the yield of the secondary molecular ion NO^- , we recently targeted various minerals (buddingtonite, phlogopite, hyalophane) with known N contents by SIMS. This study, which was funded by *Europlanet*, was carried out in collaboration with Caterina Melai and Prof. Dan Frost (University of Bayreuth), and the ultimate goal was to determine the N partition coefficient between various hydrous aluminosilicates (montmorillonite, phlogopite, phengite and serpentinites) and melt. Unfortunately, the buddingtonite crystals were too small and "flaky" to be analyzed by SIMS, and phlogopite showed a highly variable NO^- signal over the course of a 30-min analysis (i.e., with depth), suggesting that N is heterogeneously distributed within the mica crystal structure. Hyalophane, a barium-rich potassium feldspar containing ~ 0.11 wt.% N, was found to yield a very low NO^- signal, and, thus, to fall significantly to the right of the calibration line defined by the synthetic glasses (**Figure 5.2.3**). This observation is consistent with the findings of Mosenfelder et al. (2019), and suggests that the NO^- signal might be affected by the high atomic mass of Ba (the matrix contains ~ 20 wt.% BaO). The results from our hyalophane measurements emphasize the need to use matrix-matched calibrants whenever possible when analyzing N contents in particularly heavy matrices; for minerals with average molar masses close to the glasses (e.g., olivine, pyroxene, garnet, bridgmanite; Keppler et al., 2022; Li et al., 2013; Yoshioka et al., 2018; Fukuyama et al., *under review*), matrix effects are generally assumed to be minimal and are not discussed. Notably, for (Nano-)SIMS N analyses in other laboratories, N-implanted minerals and/or glasses are used as calibrants (e.g., Li et al., 2013; Fukuyama et al., 2020; Keppler et al., 2022; Regier et al., 2016; Yoshioka et al., 2018); it is unclear (to me) whether the ion yield of samples containing implanted or dissolved N is comparable or whether a significant matrix effect occurs.

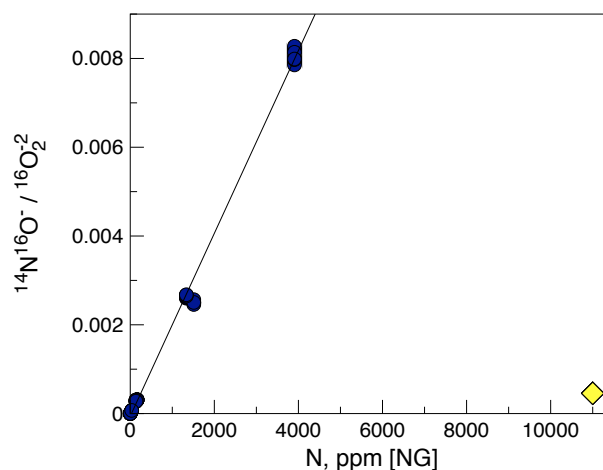


Figure 5.2.3. Relationship between the secondary ion intensity ratio $^{14}\text{N}^{16}\text{O}^- / ^{16}\text{O}_2^-$ and the known N content (determined by static noble gas mass spectrometry) of synthetic glasses (blue circles) and hyalophane (yellow diamond).

6 – N abundances and isotopic characteristics of differentiated meteorites

Differentiated achondrites ('stony meteorites') sample the silicate-dominated crust/mantle of a highly diverse set of parent bodies that experienced high degrees of melting and large-scale differentiation (Mittlefehldt, 2013). They provide a wealth of information on the chemical and physical evolution of the early solar system during the initial stages of terrestrial planet formation, as well as, in the case of martian and lunar meteorites, on subsequent planetary processes. The majority of achondrites (such as the angrites) are derived from unidentified asteroidal parent bodies, whereas the martian and lunar meteorites originate from known 'planetary' bodies, i.e., the planet Mars and the Moon. Martian meteorites are of particular value given they are the only samples of Mars currently available to study in laboratories on Earth (McSween, 1994; Udry et al., 2020). In contrast to achondrites, 'magmatic' iron meteorites are derived from the metallic cores of the earliest, differentiated planetesimals (Kruijjer et al., 2014) that were subsequently disrupted through catastrophic impacts (Benedix et al., 2013). Given that the parent bodies of achondrites and iron meteorites presumably formed at different times and locations in the protoplanetary disk – as indicated by nucleosynthetic isotopic anomalies and/or $\Delta^{17}\text{O}$ systematics (e.g., Kleine et al., 2020; Kruijjer et al., 2020; Scott et al., 2018a; Warren, 2011) – these objects may retain a record of the early chronology of volatile accretion by planetary bodies in the inner and outer solar system.

The N content and isotopic composition of various achondrite fragments, including angrites (Abernethy et al., 2018, 2013) and martian meteorites (Mathew and Marti, 2001), was previously analyzed by stepped heating/combustion extraction and static noble gas mass spectrometry. With this method, however, identifying the main N carrier phase(s) (e.g., silicate minerals, accessory phases, glass-bearing inclusions) is challenging, and, due to the possible presence of exogenous N components (i.e., SW-derived and/or cosmogenic N), determining the isotopic composition of indigenous N is not straightforward. Among the various mineral/glass phases in achondrites, melt inclusions (MIs) that were encapsulated in their host mineral during crystal growth are particularly likely to preserve the pre-eruptive volatile concentration and isotopic ratio of the parental melt because the strength of the host crystal protects inclusions from decompression and degassing during melt ascent and eruption. Consequently, MIs may also provide the best insights into the N isotopic composition of the mantles of the angrite parent body and Mars. It is, therefore, important to note that abundant glassy MIs have previously been observed in the angrites D'Orbigny and Sahara 99555 (Kurat et al., 2004; Mittlefehldt et al., 2002; Varela et al., 2003) as well as in the martian meteorite Chassigny (Floran et al., 1978; Varela et al., 2000). To improve our understanding of the source(s) and timing of volatile delivery to planetary bodies in the inner solar system, we chose to target D'Orbigny and Sahara 99555 as well as in Chassigny for the first *in situ* SIMS analyses of N abundances and isotopic ratios in achondrite MIs. These studies represented a major 'task' of my ERC project 'VOLATILIS', and they were central to Cécile Deligny's PhD thesis work, supervised by Etienne Deloule and myself.

6.1 – N abundances and isotopic compositions of melt inclusions in angrites

Angrites are a small group of mafic to ultramafic achondrites with identical oxygen isotopic compositions (Clayton and Mayeda, 1996) and similar unusual mineralogy (Mittlefehldt et al., 2002) that presumably originate from a common differentiated parent body. Their $\epsilon^{54}\text{Cr}$ – $\epsilon^{50}\text{Ti}$ anomalies and $\Delta^{17}\text{O}$ isotopic signature imply that the angrite parent body (APB) formed in the NC reservoir, sunward of Jupiter (Scott et al., 2018a; Warren, 2011, and references therein). Furthermore, ^{26}Al – ^{26}Mg and Hf–W data indicate that the APB accreted within the first ~0.4 to 1.5 Ma after CAI formation (Kleine et al., 2012; Schiller et al., 2015). D'Orbigny and Sahara 99555 are two of the oldest volcanic angrites, with Pb–Pb ages of $4,563.51 \pm 0.8$ Ma and $4,564.07 \pm 0.43$ Ma, respectively (Tissot et al., 2017). Both meteorites contain abundant MIs (Kurat et al., 2004; Mittlefehldt et al., 2002; Varela et al., 2003) (Figure 6.1.1.), and previous *in situ* nuclear microanalyses revealed that these inclusions contain up to 180 ppm N and 40–735 ppm C (Varela et al., 2003). Together with results from stepped combustion analyses of nitrogen (Abernethy et al., 2018, 2013) and SIMS analyses of hydrogen (Sarafian et al., 2017), these observations indicate that the APB accreted a significant amount of highly volatile elements (H, C N) during the earliest period of planet formation and evolution, in spite of the fact that angrites are considered to be the most (lithophile) volatile-depleted basalts in the solar system, with significantly lower Rb/Sr and K/U ratios than CI chondrites (e.g., Day and Moynier, 2014).

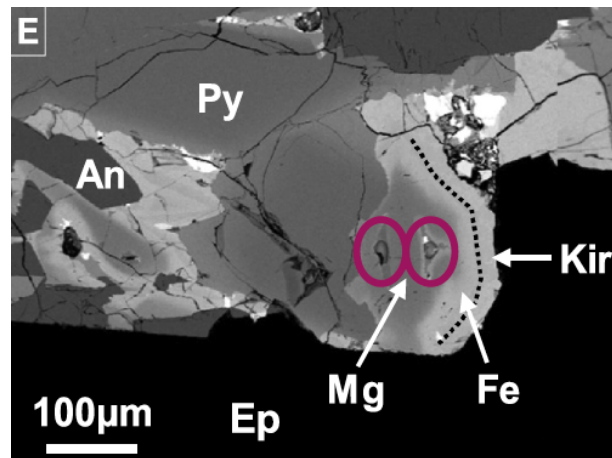


Figure 6.1.1. Backscattered electron image of D'Orbigny. An: Anorthite, Py: Pyroxene, Mg: Mg-rich olivine, Fe: Fe-rich olivine, Kir: Kirschsteinite. Pink circles indicate olivine-hosted melt inclusions that were targeted for SIMS analyses. From Deligny et al. (2021).

For this study, I first purchased a fragment of D'Orbigny for oxygen and nitrogen isotope analyses by SIMS, and we subsequently obtained additional polished sections and fragments of D'Orbigny and Sahara 99555 (i.e., from the Naturhistorisches Museum Wien and the Institut für Planetologie der Westfälischen Wilhelms-Universität Münster) for a more detailed study of the nitrogen (and hydrogen) abundance and isotopic composition of mineral-hosted MIs. We found that the most primitive (i.e., Mg-rich) melt trapped in olivine-hosted MIs of D'Orbigny records $\delta^{15}\text{N}$ values between 0 ± 25 to $+56 \pm 29$ ‰ and δD values ranging from -348 ± 53 to -118 ± 31 ‰ (Figure 6.1.2.).

These results suggest that the APB mantle source sampled by D'Orbigny contains isotopically CM-like volatiles, possibly with a contribution of hydrogen ingassed during the lifetime of the solar nebula, as indicated by the most D-depleted hydrogen isotopic ratios. The low nitrogen and hydrogen contents measured in Sahara 99555 possibly indicate that its parental melt underwent a higher degree of degassing compared to D'Orbigny or, alternatively, that the two Angrites do not sample the same volatile reservoir within the APB. Given the very old crystallization age of D'Orbigny, our findings imply that nitrogen- and water-rich material, presumably formed beyond the orbit of Jupiter, must have been present in the terrestrial planet-forming region within the first ~ 4 Ma after the formation of CAIs. Consequently, other planetary bodies that accreted early within the inner solar system are also expected to have incorporated isotopically carbonaceous chondrite-like volatiles.

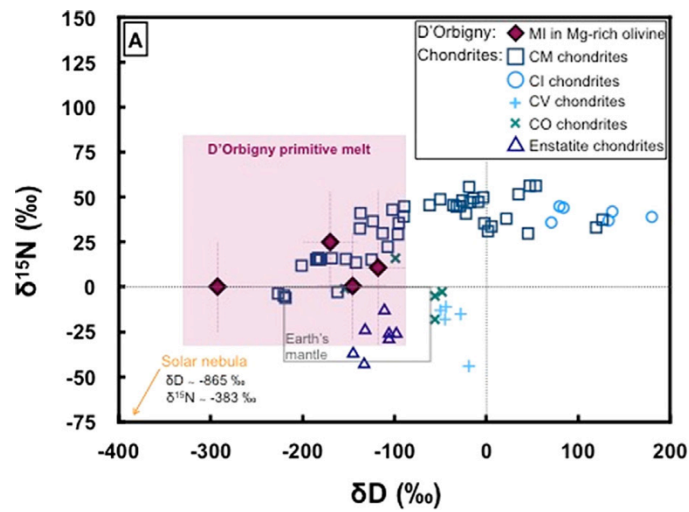


Figure 6.1.2. $\delta^{15}\text{N}$ versus δD (corrected for cosmogenic ^{15}N and D, respectively) of the least degassed melt trapped in Mg-rich olivine of D'Orbigny. The range of measured N ($n = 7$) and H ($n = 4$) isotopic ratios in the most primitive melt of D'Orbigny is indicated by the pink rectangle. The nitrogen and hydrogen isotopic compositions of carbonaceous chondrites (CM, CI, CV, and CO), enstatite chondrites as well as Earth's mantle are shown for comparison (Alexander et al., 2012; Cartigny and Marty, 2013; Grady et al., 1986; Hui et al., 2017; Kung and Clayton, 1978; Piani et al., 2020). From Deligny et al. (2021).

6.2 – N abundances and isotopic compositions of melt inclusions in martian meteorites

Martian meteorites (the so-called SNCs: Shergottites, Nakhilites, Chassignites, as well as ALH (Allan Hills) 84001 and NWA (Northwest Africa) 7064) are unique samples to study the formation, differentiation, and evolution of Mars as well as the origin and abundance of volatiles present in the martian interior (Filiberto and Schwenzer, 2018; McSween, 1994; Udry et al., 2020). To explain isotopic anomalies of $\Delta^{17}\text{O}$, $\epsilon^{50}\text{Ti}$, $\epsilon^{54}\text{Cr}$, $\epsilon^{62}\text{Ni}$, and $\epsilon^{92}\text{Mo}$ in martian meteorites, Mars is assumed to have formed from enstatite and ordinary chondrite-like materials (Brasser et al., 2018; Tang and Dauphas, 2014), likely with a small ($\sim 4\%$) contribution of carbonaceous-chondrite-like (i.e., CC-type) material from the outer solar system (Burkhardt et al., 2021). Consequently, any volatiles trapped and preserved in the martian mantle may originate from various sources in the early inner and outer protoplanetary disk.

Nitrogen contents of up to 7450 ppm were measured by nuclear reaction analysis of glassy inclusions in the martian dunite Chassigny (Varela et al., 2000), implying that a large amount of nitrogen could be trapped in Chassigny's mantle source. Mathew and Marti (2001) determined the nitrogen isotopic composition of melt-inclusion-bearing olivine separates of Chassigny by step-heating extraction and static noble gas mass spectrometry, and concluded that a $\delta^{15}\text{N}$ value of -30‰ may be characteristic of the martian mantle. This value is consistent with the isotopic composition of nitrogen in enstatite chondrites ($\delta^{15}\text{N}_{\text{EC}} = -47$ to -13‰ ; Grady et al., 1986; Kung and Clayton, 1978). In contrast, nitrogen analysis of Nakhla by stepped heating yielded $\delta^{15}\text{N}$ values between $+4.6 \pm 4.2$ and $+7.2 \pm 3.8\text{‰}$ (corrected for the cosmogenic ^{15}N contribution), suggesting that Nakhla trapped a ^{15}N -enriched atmospheric gas component, possibly during impact ejection (Mohapatra and Murty, 2003). Indeed, *in situ* analysis by the Viking lander revealed that the martian atmosphere contains 2.7 vol.% N_2 with a $\delta^{15}\text{N}$ value of $+620 \pm 160\text{‰}$ (e.g., Owen et al., 1977). The elevated N isotopic ratio of the martian atmosphere may either result from ^{14}N loss by non-thermal escape to space (McElroy et al., 1976) or from the contribution of a ^{15}N -rich component such as comets (Marty et al., 2016).

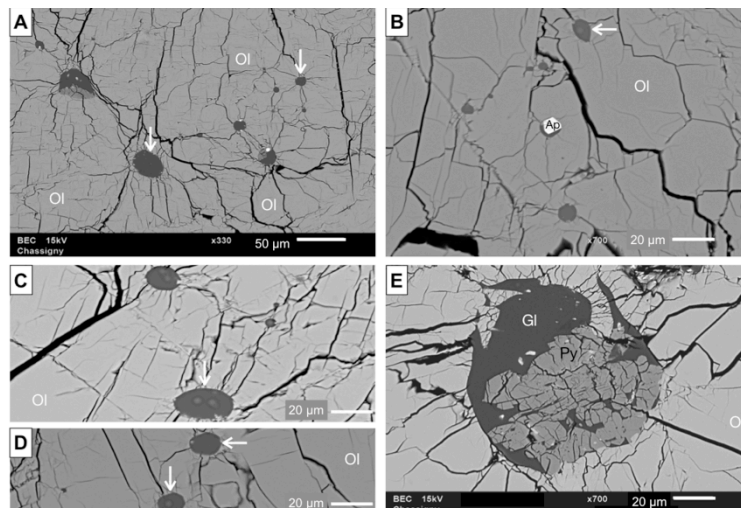


Figure 6.2.1. (A-D) Backscattered electron images of Chassigny. White arrows indicate completely glass melt inclusions that were targeted for SIMS analyses. (E) Zoom on a peculiar, partially crystallized melt inclusion. Partially crystallized melt inclusions were not analyzed by SIMS. Ap: Apatite, Gl: Glass, Ol: Olivine, Py: Pyroxene. From Deligny et al. (*under review*).

To better assess the source(s) of nitrogen trapped in the martian interior, we targeted, for the first time, pristine phases (melt inclusions and mesostasis) in Chassigny and five different nakhlites (Nakhla, NWA 998, MIL 03346, Y 000593, NWA 6148) for *in situ* measurements of their nitrogen content and isotopic ratio by SIMS (Deligny et al., *under review*). The studied nakhlites were previously analyzed for their hydrogen isotopic ratios – as well as their water, major element, and trace element content – by Peslier et al. (2019). The $\delta^{15}\text{N}$ values Chassigny MIs (Figure 6.2.1) range from -35 ± 41 to $+73 \pm 36\text{‰}$ (corrected for cosmogenic ^{15}N based on published CRE ages; Figure 6.2.2). The estimated N isotopic signature of the primitive melt, prior to degassing of N_2 or NH_3 , is $\sim 0 \pm 32\text{‰}$. The mesostasis of nakhlites records $\delta^{15}\text{N}$ values between -30 ± 37 and $+348 \pm 43\text{‰}$ (Figure

6.2.2.). The highest $^{15}\text{N}/^{14}\text{N}$ ratios ($\delta^{15}\text{N} > 150 \text{ ‰}$) cannot be explained by degassing and likely result from interactions of the mesostasis melt with the martian atmosphere during impact ejection. In contrast, the $\delta^{15}\text{N}$ values ($+25 \pm 42$ and $+77 \pm 19 \text{ ‰}$) of two melt inclusions in the nakhlite Y 000593 are comparable to those of Chassigny, further confirming that the melt trapped in these meteorites likely samples a common volatile reservoir. Overall, the new results indicate that the chassignite-nakhlite reservoir did not inherit nitrogen from the solar nebula but, instead, from isotopically chondritic-like materials. Interestingly, based on recent high-precision analyses of krypton and xenon isotopes in Chassigny, Péron and Mukhopadhyay (2022) concluded that heavy noble gases in the martian interior also have a chondritic (non-solar) origin. These findings further confirm that planetary bodies in the inner solar system accreted chondritic nitrogen and noble gases during the first few millions years of solar system history. However, based on nitrogen isotope measurements alone, we cannot distinguish between incorporation of 'chondritic' volatiles from NC-type material, formed in the inner solar system, or from CC-type material scattered inwards due to the growth and/or gas-driven migration of the giant planets (Raymond and Izidoro, 2017).

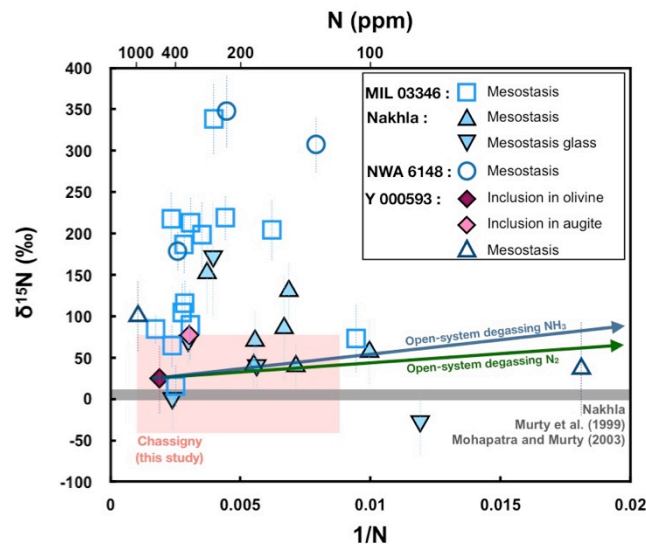


Figure 6.2.2. $\delta^{15}\text{N}$ (corrected for cosmogenic ^{15}N) as a function of the inverse of the nitrogen concentration (bottom x axis) and the nitrogen concentration (in ppm; top x axis) of nakhlites. Trajectories for open-system (Rayleigh distillation) degassing of N_2 and NH_3 are indicated in green and blue, respectively. The range of nitrogen contents (corrected for olivine overgrowth) and $\delta^{15}\text{N}$ values for Chassigny is indicated by the pink rectangle. Error bars indicate 2σ uncertainties. From Deligny et al. (*under review*).

6.3 – N isotopic compositions of iron meteorites

To better understand how the distribution of N (and its carrier phases) evolved in space and time within the earliest stages of the protoplanetary disk, I recently turned my attention to metal-rich meteorites. 'Magmatic' iron meteorites, which are predominantly composed of Fe-Ni alloy⁸, are considered to originate from the metal cores of small, differentiated, and subsequently disrupted

⁸ Most iron meteorites are characterized by an intergrowth of two Fe-Ni alloy phases, kamacite and taenite. Kamacite is ferritic iron ($\alpha\text{-Fe}$) with 5.5–7.5 wt% Ni, whereas taenite is an austenitic phase ($\gamma\text{-Fe}$) with >25 wt% Ni in solid solution (Buchwald, 1975).

planetesimals. This interpretation is mainly based on compositional trends of the volatile siderophile elements Ge and Ga relative to Ni and Ir (or Au), which are consistent with fractional crystallization of a slowly cooling metal melt body at considerable depth (Scott, 1972; Scott and Wasson, 1975). Cooling rates indicate that core formation occurred in bodies 5–200 km in diameter (Chabot and Haack, 2021; Mittlefehldt et al., 1998), although some iron meteorite parent bodies may have had diameters of 500–1000 km (Yang et al., 2007). Based on chemical, structural, and mineralogical properties and CRE ages, 11 different genetic groups of 'magmatic' iron meteorites (IC, IIAB, IIC, IID, IIF, IIG, IIIAB, IIIE, IIIF, IVA, IVB) have been identified, each presumably sampling the core of a different parent body (Scott and Wasson, 1975; Wasson, 1970, 1969, 1967; Wasson and Kimbrell, 1967). 'Ungrouped' irons are an additional diverse set of samples whose chemical compositions do not match any of the 11 established groups; they may represent fragments of ≥ 50 distinct, poorly sampled planetesimal cores (Scott, 1979). Two other iron meteorite groups are 'non-magmatic' or 'silicate-bearing' (IAB, IIE); their origin is uncertain and may be related to partial differentiation and/or impact melting and mixing (Benedix et al., 2013, 2000; Mittlefehldt et al., 1998). Recent high-precision geochemical datasets (i.e., nucleosynthetic Mo-Ru-Ni isotopic anomalies) have revealed that some iron meteorite groups are isotopically similar to non-carbonaceous (NC) chondrites (i.e., ordinary and enstatite chondrites), whereas others isotopically resemble carbonaceous chondrites (CC) (Bermingham et al., 2018; Budde et al., 2016; Burkhardt et al., 2011; Kruijjer et al., 2017b; Nanne et al., 2019; Spitzer et al., 2020). Since Hf–W model ages and thermal modeling of bodies internally heated by ^{26}Al decay imply that the parent bodies of NC- and CC-type iron meteorites accreted contemporaneously within the first ~ 1 Ma of solar system history (Spitzer et al., 2021), iron meteorites may preserve a record of the abundance and isotopic composition of N (and its carrier phases) within the NC and CC reservoirs during the first stages of planetary formation, prior to the accretion of the parent bodies of chondrites that are represented in our global meteorite collection (e.g., Desch et al., 2018; Kruijjer et al., 2020, and references therein).

Given that N can be (moderately) siderophile during metal-silicate fractionation over a certain range of $f\text{O}_2$ conditions (Dalou et al., 2017; Grewal et al., 2019; Kadik et al., 2013, 2011; Roskosz et al., 2013; Speelmanns et al., 2019, 2018), iron meteorites contain a significant, but highly variable, amount of N (i.e., ≤ 1 to 120 ppm N; **Figure 6.3.1.**). Therefore, these objects may potentially retain a record of the spatial and temporal evolution of N isotopes during the earliest stages of planetary accretion and differentiation. Irons record a remarkably wide range of $\delta^{15}\text{N}$ values between -91.8‰ and $+153.2\text{‰}$, as determined in several laboratories by SIMS or static noble gas mass spectrometry (**Figure 6.3.1.**; Mathew et al., 2000; Murty et al., 2019; Ponganis and Marti, 2007; Prombo and Clayton, 1993; Sugiura, 1998; Sugiura et al., 2000). Several authors have previously argued that secondary modifications or parent body processes are unlikely to have produced N isotopic variations of $\sim 250\text{‰}$ in iron meteorites or planetesimal cores. Grewal et al. (2021b) concluded that the

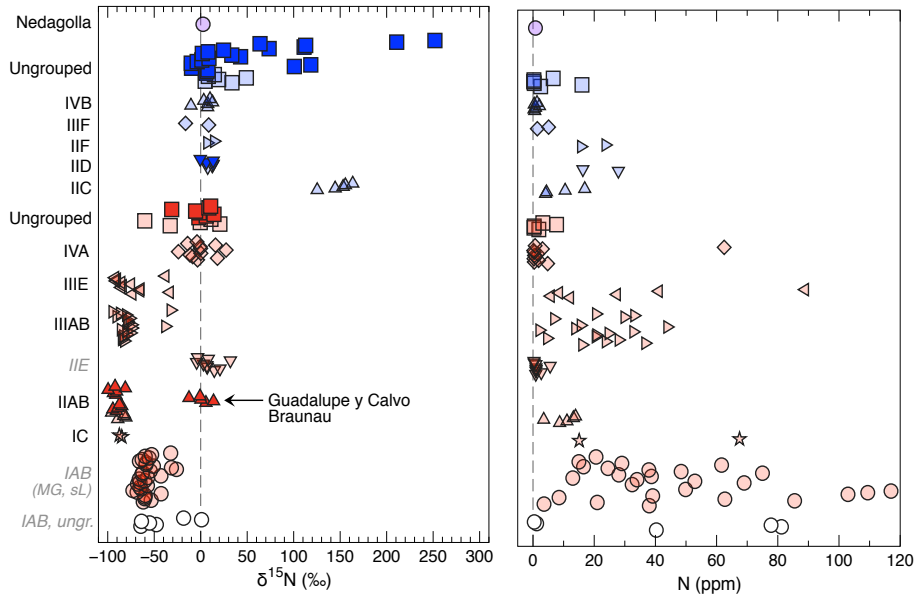


Figure 6.3.1. N isotopic ratios (left) and abundances (right) of iron meteorites (IAB and IIE irons being 'non-magmatic'). NC- and CC-type irons are shown in red and blue, respectively. Data sources: Franchi et al., 1993; Mathew et al., 2000; Murty et al., 2019; Pepin and Becker, 1982; Ponganis and Marti, 2007; Prombo and Clayton, 1993; Sugiura, 1998; Sugiura et al., 2000a. N isotopic compositions of ungrouped, IIAB, and IID irons measured by Füri et al. (*in prep.*) are shown in darker colors; associated N abundances could not be determined because the 20-year-old CO_2 laser did not permit the quantitative extraction of N from the metal fragments.

incorporation of isotopically light nebular N ($\delta^{15}\text{N}_{\text{solar}} = -383 \pm 8$ ‰; Marty et al., 2011), either before/during parent body accretion or upon disruption, can be ruled out as the cause of low $\delta^{15}\text{N}$ values in NC-type irons because the partial pressure of N in nebular gas is too low to ingest significant amounts of N (≥ 0.1 ppm) into Fe-Ni alloys, consistent with Fegley's (1983) conclusions based on thermodynamic equilibrium calculations. However, the presence of solar noble gases in the ungrouped iron meteorite Washington County suggests that some planetesimal cores may contain solar-wind-derived gases carried by irradiated precursors (Becker and Pepin, 1984; Hintenberger et al., 1967; Vogt et al., 2021). Cosmic-ray-induced spallation effects on N abundances and isotopic ratios in irons are negligible in most cases, despite their prolonged exposure histories in space (e.g., $\sim 675 \pm 100$ Ma and 450 ± 100 Ma for IIIAB and IVA irons, respectively; Voshage and Feldmann, 1979); because cosmogenic ^{15}N is predominantly produced by reactions with oxygen (Mathew and Murty, 1993), the N isotopic ratios of metal phases are not demonstrably affected by spallation, although spallation effects in irons containing numerous silicate inclusions can be pronounced (Franchi et al., 1993; Mathew et al., 2000). Finally, Prombo and Clayton (1993) argued that the absence of a correlation between the $\delta^{15}\text{N}$ values and the Ni or Ir contents of IIAB and IIIAB irons implies that N isotopic ratios are not significantly modified during the fractional crystallization of liquid metal. Consequently, by assuming that the N isotopic compositions of iron meteorites reflect those of their parent bodies, Rubin (2018), Scott et al. (2018b), and Grewal et al. (2021) concluded the N isotopic ratios of iron meteorites record a NC-CC dichotomy because NC- and CC-type iron meteorites have negative and positive $\delta^{15}\text{N}$ values, respectively. This dichotomy implies that the earliest planetesimals in the inner and outer protoplanetary disk accreted isotopically distinct N (Grewal et al., 2021), and that the

transport and mixing of N carrier phase(s) (possibly including ices, organics, and/or reduced phases such as nitrides) between the NC and CC reservoirs must have been inhibited during the first stages of planetary accretion.

To further investigate the N isotopic composition of iron meteorites, I recently analyzed 22 irons (IIAB, IID, ungrouped; **Figure 6.3.1.**) by CO₂ laser heating and static noble gas mass spectrometry. (I note here that Christoph Burkhardt from the University of Münster sent me the samples for this study in 2018, but, due to the technical issues mentioned in **Chapter 5**, they could only be analyzed in 2021.) The main limitation of this (low-blank) approach is that the metal fragments could not be melted with the 20-year-old CO₂ laser at CRPG's noble gas facility; nonetheless, the isotopic ratio of N extracted by repeated heating of a given sample did not vary significantly, indicating that there is no 'distillation' effect. Our data confirm that iron meteorites record a wide range of $\delta^{15}\text{N}$ values, between -100 and $+250$ ‰, and that any contributions from solar or cosmogenic N are negligible (as implied by the absence of measurable quantities of solar and cosmogenic noble gases). The IIAB irons Braunau and Guadaloupe y Calvo are isotopically distinct from the other members of their group. Overall, I conclude that the available data suggest that there is no clear N isotope dichotomy between NC- and CC-type irons, in contrast to the recent findings of Grewal et al. (2021). Although the lowest $\delta^{15}\text{N}$ values, around -90 ‰, are only observed in NC-type irons and high $\delta^{15}\text{N}$ values exceeding $+100$ ‰ only in CC-type irons, many NC- and CC-type iron meteorite groups have overlapping $\delta^{15}\text{N}$ values (**Figure 6.3.1.**); even among those formed in the CC reservoir, only the IIC and a few ungrouped irons have $\delta^{15}\text{N} > +30$ ‰. Importantly, the $\delta^{15}\text{N}$ signatures of NC-type IVA and ungrouped irons, whose parent bodies presumably accreted in the inner solar system, indicate that isotopically chondritic-/terrestrial-like N must already have been present in the terrestrial planet-forming region during the first ~ 1 Ma of solar system history. I am hoping to soon complete an article presenting the N–noble gas (–Mo–Ru–W) results and interpretation thereof, in collaboration with Christoph Burkhardt and Fridolin Spitzer (University of Münster).

6.4 – Conclusions and outlook

The isotopic composition of nitrogen retained in the least-degassed melt pockets in angrites (D'Orbigny; **Figure 6.1.2.**) and martian meteorites (Chassigny and the nakhlite Y 000593; **Figure 6.2.2.**) indicates that the APB and Mars accreted 'chondritic' nitrogen during the earliest stages of planet formation in the inner solar system. Similarly, recent high-precision analyses revealed that krypton (and xenon) isotopic ratios of Chassigny are chondritic (Péron and Mukhopadhyay, 2022). Thus, even though the APB and Mars both presumably formed prior to the complete dissipation of nebular gas (within ≤ 5 Ma after CAI formation; **Figure 4.3.**; e.g., Borlina et al., 2022; Wang et al., 2017), nitrogen and noble gases were predominantly derived from non-solar sources. Data from iron meteorites also imply that differentiated planetesimals in the inner and outer solar system incorporated non-solar nitrogen during the first ~ 1 Ma of solar system history – provided that the nitrogen isotopic

composition of iron meteorites reflects that of the bulk materials that composed their parent bodies. It is still debated, however, how the isotope distribution of nitrogen (and its carrier phases) evolved in space and time within the earliest stages of the protoplanetary disk. My proposed project 'IRONIS' (under call ERC-2022-CoG) – *Light elements in irons and metal-rich meteorites: Their isotopic distribution and evolution in the protoplanetary disk* – aims to address these fundamental questions based on new isotopic analyses of nitrogen in irons and other Fe-Ni alloy-rich meteorites and experimental simulations (see **Chapter 8** for details).

An important caveat is that the nitrogen isotopic composition of achondrites may not be representative of their parent bodies' interior because nitrogen isotopes may have been fractionated or modified by 'magmatic' and 'exogeneous' processes. Although in our studies of MIs in angrites and martian meteorites we tried to assess the effects of degassing on the nitrogen isotopic composition of the trapped melt, the degassing species (e.g., N_2 vs. NH_3) and the mode of degassing (open vs. close system, equilibrium vs. kinetic) are unknown. Similarly, we corrected the measured nitrogen isotopic ratios for spallation effects (i.e., for the production of cosmogenic ^{15}N during space exposure) using published ^{15}N production rates and exposure ages, but the irradiation histories of the studied sub-samples are not well constrained. I should also be noted that Chassigny and nakhlites are severely shocked meteorites (and MIs in Chassigny are surrounded by numerous radial fractures; **Figure 6.2.1.**), and the initial nitrogen content and isotopic composition of the mesostasis in nakhlites appears to have been modified by interaction with atmospheric gases during shock melting upon ejection. A Mars sample-return mission is, therefore, crucial to collect specific, pristine samples from selected areas of interest on Mars, and, ultimately, to improve our understanding of the origin of nitrogen trapped in the interior of Mars.

One key question remains: were N isotopes in planetary mantles fractionated during planetary processes such as magma ocean degassing, magma ocean crystallization, and/or core-mantle differentiation? Constraining the effect(s) of these major processes is crucial for determining whether N in Earth's mantle, as well as in the mantles of other planetary bodies, has preserved its original isotopic signature. As mentioned in **Chapter 4**, high-pressure and high-temperature experiments have already provided some insights on the magnitude of N isotope fractionation during magma ocean degassing (Dalou et al., 2022) and core formation (**Figure 4.4.**; Dalou et al., 2019a; Li et al., 2016; Shi et al., 2022), but these experimentally *and* analytically challenging studies have provided controversial results. It should be pointed out that planetary processes have likely also affected the D/H ratio of 'water' trapped in planetary interiors, yet this key issue is rarely addressed.

7 – Volatiles (H, N, noble gases) in samples returned from the Moon

7.1 – Hydrogen components in lunar samples

The Moon is thought to have formed from a hot, partially vaporized circum-terrestrial disk generated by a giant impact between the proto-Earth and a planetesimal named 'Theia' (e.g., Canup, 2012, 2004; Hartmann and Davis, 1975). This formation process was likely responsible for the Moon's depletion in volatile elements (e.g., K) compared to Earth, although the mechanisms by which volatiles were lost from the Moon-forming material are still highly debated (e.g., Canup et al., 2015; Charnoz and Michaut, 2015; Hauri et al., 2015; Nakajima and Stevenson, 2018; Righter, 2019). The apparent absence of 'indigenous' (i.e., primordial or magmatic) hydrogen noted during the earliest studies of Apollo samples (Epstein and Taylor, 1972; Ringwood and Kesson, 1977) seemed to support the notion of a completely dry Moon (Taylor et al., 2006). However, thanks to technological advances in lab instrumentation such as SIMS, detection limits for hydrogen have significantly improved, which lead to the discovery of indigenous H-bearing species (H_2 , OH and/or H_2O , in the following referred to as 'water') in *i*) lunar pyroclastic glasses (Saal et al., 2008) and olivine-hosted melt inclusions therein (Hauri et al., 2011), *ii*) apatite (McCubbin et al., 2010), *iii*) olivine-/ilmenite-hosted melt inclusions in mare basalts (Hu et al., 2021; Singer et al., 2017), and *iv*) plagioclase in ferroan anorthosites (Hui et al., 2013). Together with the detection of water ice in permanently shadowed polar regions of the Moon (Feldman et al., 1998), these findings have led to a paradigm shift in our knowledge and understanding of the water inventory of Earth's sole natural satellite. The new data have stimulated new investigations of the origin of volatiles within the Earth-Moon system, as well as of the physical and chemical conditions that prevailed in the post-impact protolunar disk, with different models suggesting that water and other volatile elements either (partially) survived in the disk or were accreted after the giant impact that led to the formation of the Moon (e.g., Barnes et al., 2016; Hauri et al., 2015; Nakajima and Stevenson, 2018; Pahlevan et al., 2016).

Apollo samples that presumably sample the Moon's mantle record a wide range of δD values between < -500 ‰ and $\geq +1000$ ‰ (see McCubbin et al., 2015 for a review), which have been interpreted to reflect hydrogen or water contributions from various sources, such as the solar nebula, carbonaceous chondrites, and/or comets to the lunar interior (e.g., Anand et al., 2014; Barnes et al., 2016, 2014; Desch and Robinson, 2019; Füre et al., 2014; Greenwood et al., 2011; Hu et al., 2021; Hui et al., 2017; Robinson et al., 2016; Saal et al., 2013; Sharp, 2017; Singer et al., 2017; Stephant et al., 2020; Tartèse et al., 2013). However, measured D/H ratios of available lunar samples do not directly reflect those of the lunar mantle source. In addition to isotopic fractionation induced by magmatic processes (e.g., degassing; Hu et al., 2021; Saal et al., 2013; Stephant et al., 2020; Tartèse et al., 2013), the D/H ratio of water in virtually all samples collected during the Apollo, Luna, and Chang'e-5 missions has been modified by irradiation processes. Since the Moon's surface lacks full atmospheric shielding and magnetic field protection against the solar wind (SW) as well as against high-energy

galactic (GCR) and solar cosmic rays (SCR), SW-derived gases are implanted into the top few tens of nanometers of any regolith grain or rock exposed to the lunar surface environment (e.g., Hashizume et al., 2000), and cosmic-ray induced spallation reactions – triggered by GCR and SCR particles that can penetrate lunar matter to depths of several meters and a few centimeters, respectively – are important sources of cosmogenic (or 'spallogenic') nuclides, such as deuterium (^2H or D) and noble gases (e.g., ^3He , ^{21}Ne , ^{38}Ar), in lunar samples with long CRE ages (Rao et al., 1994; Reedy, 2015, 1981). Importantly, a contribution of SW-implanted hydrogen to the measured water abundances and D/H ratios can generally be ruled out because all recent hydrogen isotope measurements of lunar samples have been carried out *in situ* by SIMS, in the interior of lunar volcanic glass beads (Füre et al., 2014; Saal et al., 2013, 2008) or within mineral grains and melt inclusions that were never directly exposed to SW irradiation (e.g., Barnes et al., 2014, 2013; Boyce et al., 2010; Hu et al., 2021; Hui et al., 2017; Robinson et al., 2016; Saal et al., 2013; Singer et al., 2017; Stephant et al., 2020; Tartèse et al., 2013; Tartèse and Anand, 2013). In contrast, cosmic-ray-produced deuterium is expected to contribute significantly to the D/H ratio of water-poor lunar samples that experienced long exposure to cosmic rays at the surface of the Moon. Consequently, accurate knowledge of the samples' CRE age and of the cosmogenic D production rate (P_D) is critical for correcting measured D/H ratios for the cosmogenic contribution, and, ultimately, for comparing lunar hydrogen isotope signatures with those of potential solar system sources (i.e., solar, chondritic, cometary, terrestrial).

Merlivat et al. (1976) estimated the GCR-induced production of cosmogenic deuterium to be $0.92 \times 10^{-12} \text{ mol(g rock)}^{-1}\text{Ma}^{-1}$, based on the abundances of water, hydrogen, and deuterium in eight sub-samples from different depths of mare basalt 70215. This P_D value relies on the assumption that the measured deuterium is a mixture between D generated by the reduction of terrestrial water during the experimental process and cosmogenic D, which has been produced *in situ* by spallation reactions during space exposure. Recently, Greenwood et al. (2018) argued that mare basalt 70215 analyzed by Merlivat et al. (1976) contains indigenous OH (in addition to water from terrestrial contamination and cosmogenic D), rendering their P_D estimate unreliable. Nonetheless, from theoretical calculations, Reedy (1981) derived a similar value (i.e., $\sim 1200 \text{ atoms/min/kg}$ or $1 \times 10^{-12} \text{ mol(g rock)}^{-1}\text{Ma}^{-1}$) for the GCR production of D in lunar rocks from the target elements O, Mg, Al, Si, and Fe for the top 40 g/cm^2 of shielding; this author also argued, however, that the additional production of D from SCRs would significantly increase the total production rate.

To verify the accuracy of the previously published P_D values, I designed a study specifically aimed at determining the production rate of cosmogenic D at the Moon's surface through analyses of olivines from eight Apollo 12 and 15 mare basalts (Füre et al., 2017). The olivine-rich mare basalts were allocated to me for this project by NASA's Curation and Analysis Planning Team for Extraterrestrial Materials (CAPTEM), and the project was funded by the Programme National de Planétologie (PNP-INSU) and the Conseil Régional de Lorraine. By coupling two high-precision

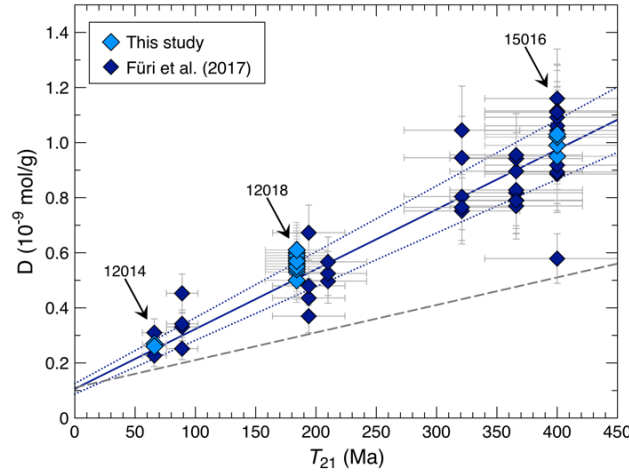


Figure 7.1.1. Deuterium abundances in olivines (in nmol/g) as a function of the CRE ages derived from the $^{21}\text{Ne}_{\text{cosm}}$ concentrations in mare basalt fragments (T_{21}). The solid line indicates the D production rate of $(2.17 \pm 0.11) \times 10^{-12} \text{ mol(g rock)}^{-1}\text{Ma}^{-1}$ derived by Füri et al. (2017), whereas the dashed line represents the value of $1 \times 10^{-12} \text{ mol(g rock)}^{-1}\text{Ma}^{-1}$ from Merlivat et al. (1976) and Reedy (1981). From Füri et al. (2020).

analytical techniques – SIMS and CO_2 laser extraction-static mass spectrometry – I was able to determine the deuterium content of individual olivine grains together with the CRE age (i.e., the total duration of irradiation by cosmic rays at the Moon's surface) of their host rocks. The data revealed that the amount of D detected in the olivines increases linearly with increasing ^{21}Ne exposure ages, consistent with a production rate of $2.17 \times 10^{-12} \text{ mol(g rock)}^{-1}\text{Ma}^{-1}$ (Figure 7.1.1). This value is more than twice as high as the previous estimates for the production of D by galactic cosmic rays, indicating that for water-poor lunar samples, corrected D/H ratios have been severely overestimated. Alternatively, the presence of additional deuterium produced by SCRs in the studied olivines could have increased the abundances of cosmogenic D.

To better assess the importance of SCRs and GCRs for the production of cosmogenic deuterium in lunar samples, I determined the deuterium content of olivine and pyroxene grains extracted from different depths (0 to ≥ 4.8 cm) within Apollo olivine basalt 12018 by SIMS (Figure 7.1.2.) (Füri et al., 2020). In parallel, I analyzed the noble gas (He-Ne-Ar) contents and isotope ratios of ten bulk rock fragments by CO_2 laser extraction static mass spectrometry to quantify the abundances of cosmogenic noble gas nuclides (^3He , ^{21}Ne , ^{38}Ar) at each depth and to constrain the irradiation conditions and duration. Given that these samples cover the entire depth range (i.e., the topmost 1–2 cm) in which SCR nuclides can be produced during exposure to cosmic rays, I expected to find a depth-dependent concentration profile for cosmogenic D, ^3He , ^{21}Ne , and ^{38}Ar . However, abundances of these nuclides are constant with depth (Figure 7.1.2.), and neon isotope ratios ($^{20}\text{Ne}/^{22}\text{Ne}$ and $^{21}\text{Ne}/^{22}\text{Ne}$) are distinct from the isotope signature of neon produced by SCRs. Consequently, cosmogenic deuterium and noble gas nuclides in the Apollo 12018 rock fragments and minerals must have predominantly been produced by GCRs during prolonged (i.e., 184 ± 26 Ma), and possibly complex, exposure at the lunar (near-) surface. Although the effects of SCRs on the production rate of D cannot be evaluated, this dataset confirms the P_D value of $(2.17 \pm 0.11) \times 10^{-12}$

mol(g rock)⁻¹Ma⁻¹ from my previous study (**Figure 7.1.1.**; Füri et al., 2017). This value can be used to correct the D/H ratio of 'water' (i.e., hydrogen) in olivine and pyroxene grains that were irradiated by GCRs on the Moon, provided their CRE ages are well established; however, applying the same production rate to water-poor minerals with a different composition (e.g., apatite), and whose exposure history is unknown, will likely lead to misinterpretation of the resulting hydrogen isotope ratios.

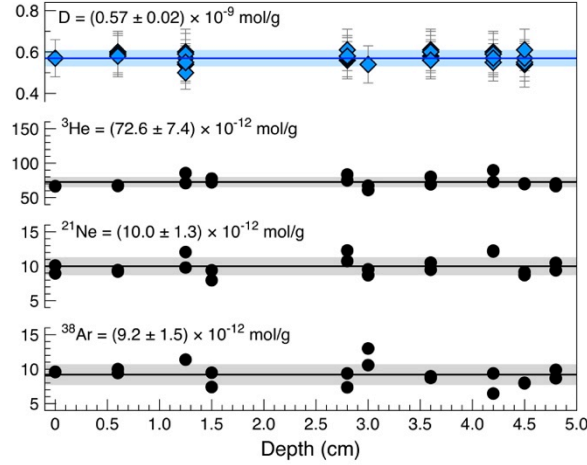


Figure 7.1.2. Deuterium concentration in Apollo 12018 olivines and pyroxenes, as well as ³He_{cosm}, ²¹Ne_{cosm}, and ³⁸Ar_{cosm} concentrations in rock fragments (duplicates at each depth), as a function of depth below the surface. Average values (solid lines) and their 1σ standard deviations (shaded areas) are indicated for each nuclide. Uncertainties (2σ s.d.) of measured noble gas contents are smaller than symbol sizes. From Füri et al. (2020).

Whereas the two studies described above showed that olivine in lunar mare basalts contains no detectable indigenous 'water' (Füri et al., 2020, 2017), Saal et al. (2008) and Hauri et al. (2011) found clear evidence for the presence of lunar water in pyroclastic glass beads and olivine-hosted melt inclusions therein. To better assess the proportion of indigenous, solar, and cosmogenic hydrogen trapped in high-Ti ('orange') volcanic glass beads collected during the Apollo 17 mission, we coupled SIMS measurements of water abundances and D/H ratios with CO₂ laser extraction static mass spectrometry analyses of noble gases (He, Ne, Ar) (Füri et al., 2014; see **Figure 3.5.** in **Chapter 3**). To correct the measured D/H ratios for the contribution of cosmogenic D, we initially used the P_D value of $\sim 1 \times 10^{-12}$ mol(g rock)⁻¹Ma⁻¹ from Merlivat et al. (1976) and Reedy (1981). We then concluded that the corrected δD values are anti-correlated with the water content, consistent with extensive hydrogen isotope fractionation during kinetic H₂ loss from a lunar melt with an inferred initial isotope signature on the order of ~ 100 ‰ and a water content of 100–300 ppm. However, by using our new P_D value (Füri et al., 2017), we found that the hydrogen isotopic signatures of 74002 glasses no longer reflect a H₂-degassing process. Instead, the Apollo 17 orange glasses and olivine-hosted melt inclusions fall onto a mixing line between solar hydrogen (D/H = $(25 \pm 5) \times 10^{-6}$; Robert, 2006) and isotopically heavier lunar 'water' (D/H = $(1.98 \pm 0.06) \times 10^{-4}$ or δD = 274 ± 42 ‰) (**Figure 7.1.3.**). Thus, the most primitive Apollo 17 high-Ti melts point to a δD value of 274 ± 42 ‰ for lunar water, provided that they retain the original pre-eruptive isotope ratio; this value is consistent with a

carbonaceous chondrite heritage (Alexander et al., 2012; Barnes et al., 2016; Saal et al., 2013). It is noteworthy that ilmenite-hosted melt inclusions in young mare basalts returned by the Chang'e-5 mission show a wide range of δD values between -330 ± 190 ‰ and $+869 \pm 230$ ‰ (Hu et al., 2021); assuming that the lowest values (i.e., the values least affected by degassing) reflect the isotopic signature of water in the Chang'e-5 mantle source, these results may indicate that water in the lunar mantle is isotopically heterogeneous.

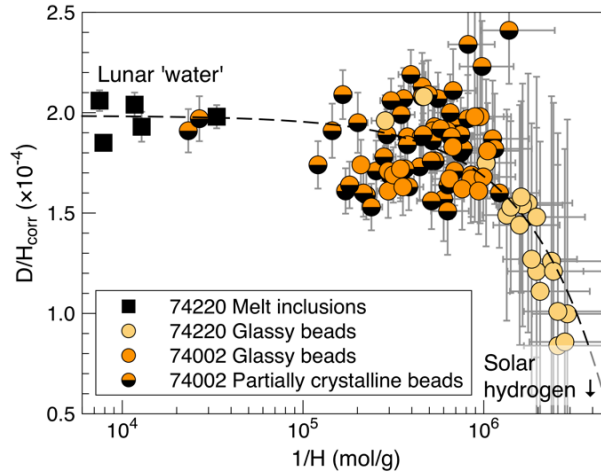


Figure 7.1.3. Hydrogen isotope ratios – corrected for the cosmogenic contribution using a P_D value of $(2.17 \pm 0.11) \times 10^{-12} \text{ mol(g rock)}^{-1}\text{Ma}^{-1}$ – as a function of the inverse of the hydrogen concentration in Apollo 17 high-Ti ('orange') volcanic glass beads (74220; Saal et al., 2013, 74002; Füre et al., 2014) and olivine-hosted melt inclusions (Saal et al., 2013). From Füre et al. (2017).

7.2 – Indigenous noble gases in lunar volcanic glasses?

The presence of indigenous water (see previous section) and other highly volatile elements (F, S, Cl, and C; Wetzel et al., 2015) in lunar volcanic glasses returned by the Apollo missions revealed that the formation and evolution of the Moon involved processes that allowed for the accretion and retention of the most volatile elements in the solar system. Although the source and timing of volatile accretion is still debated (e.g., Barnes et al., 2016; Hauri et al., 2015), these findings raise the question of whether the lunar mantle contains indigenous noble gases that were supplied to the growing Moon by the delivery of volatile-rich chondritic/cometary matter or were inherited from the proto-Earth following the giant impact. Lakatos et al. (1973) proposed that green glass spherules from Apollo sample 15426 contain solar-like noble gases that may be of primordial origin. Therefore, I targeted twelve single 15426 green glass beads (between 13 and 25 μg in mass) for noble gas analyses by CO_2 laser extraction, in collaboration with Alberto Saal (Brown University) (Füre et al., 2018b). We found that the noble gas content of the glass beads varies by two orders of magnitude (Figure 7.2.1.), consistent with CRE ages ranging from 87 ± 9 to 347 ± 73 Ma in most cases. Two gas-rich glass beads stand out with extremely long CRE ages between 1503 ± 227 and 2139 ± 303 Ma. This indicates that individual glass beads experienced highly variable irradiation histories at the lunar surface as a result of intense regolith stirring by impact gardening. The two glass spherules with the highest He–Ne–Ar

abundances released isotopically solar-like neon and argon at high temperatures. It cannot be ruled out that these volume-correlated gases are of indigenous origin. In this case, our data would suggest that the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio of the lunar mantle ($^{20}\text{Ne}/^{22}\text{Ne}_{154256} = 11.41 \pm 0.04$) is comparable to, but slightly lower than, that of the terrestrial upper mantle ($^{20}\text{Ne}/^{22}\text{Ne}_{\text{MORB}} \approx 12.5$; e.g., Péron et al., 2019). However, the amount of solar-like Ne and Ar released during melting of the two green glass beads is several orders of magnitude greater than the Ne-Ar abundances in the 2PID43 popping rock, which has been interpreted to be the best preserved sample of undegassed melt derived from the terrestrial upper mantle (Moreira et al., 1998). It appears unlikely that *i*) lunar magmas escaped degassing, and *ii*) the lunar mantle contains a larger amount of neon and argon than the terrestrial mantle, given the Moon's general volatile depletion compared to Earth (Hauri et al., 2015). In light of these caveats, the noble gas characteristics of the He–Ne–Ar-rich 15426 green glasses are best explained by inward diffusion of implanted SW-derived gases – from the surface of the spherules into their interior – during prolonged space exposure. Interestingly, Will et al. (2022) recently argued that black ("magmatic") glass in LaPaz Icefield lunar meteorites contains indigenous solar-type helium and neon; furthermore, they concluded that these noble gases were inherited from Earth's mantle during the Moon-forming impact and accumulated in the incompatible element-enriched ("KREEP") reservoir. Consequently, it cannot be ruled out that the Moon's interior retains indigenous noble gases.

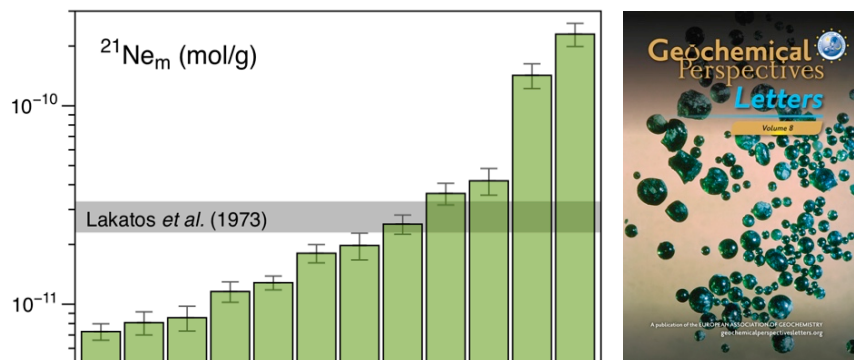


Figure 7.2.1. Left: Total ^{21}Ne abundances of twelve single 15426 green glass beads. The ^{21}Ne concentration range reported by Lakatos et al. (1973) for five grain size fractions and two large single spherules is indicated for comparison. From Füri et al. (2018b). Right: Cover of Volume 8 of *Geochemical Perspective Letters*.

7.3 – International Lunar Research Team (ILRT)

The China National Space Administration (CNSA) recently successfully completed several lunar missions, including Chang'e-3 in Mare Imbrium and Chang'e-4 on the lunar farside, and additional missions are planned for the near future. In 2020, Chang'e-5 returned the first samples from the surface of the Moon since the Soviet Union's Luna 24 mission in 1976. The European Space Agency (ESA) is also planning a robotic lander mission near the South Pole. To identify areas where Chinese and European scientists could establish new partnerships and to reinforce existing ones, several workshops were organized: *i*) "Chinese lunar samples workshop" (Beijing, August 2017), *ii*)

"CNSA-ESA workshop on Chinese-European cooperation in lunar science" (Amsterdam, July 2018), and *iii*) "CNSA-ESA international lunar research team workshop" (Zhuhai, July 2019). At these three workshops, I presented the analytical capabilities of CRPG's noble gas facility, and I summarized our findings on lunar volatiles. In 2019, both agencies tasked their respective lunar science communities to identify common interests and to define potential science objectives and possible technical implementations and associated requirements that can be conducted/implemented on and in preparation of an international lunar research station (ILRS). Several working groups, composed of European and Chinese scientists and led by two working group chiefs, were established. Together with Dr. Dunyi Liu, I chaired the working group "Samples and Joint Virtual Laboratory". After numerous virtual meetings and time-consuming discussions, the ILRT members submitted their report in October 2020. The ILRT was then closed, and we have not heard back from ESA or CNSA since. Nonetheless, several European laboratories have since then participated in a consortium study of the lunar meteorite NWA 12008; at CRPG's noble gas facility, we determined the N-noble gas isotopic composition of two meteorite fragments. The ultimate purpose and outcome of this multi-laboratory, multi-isotope study remains to be determined.

7.4 – Conclusions and outlook

Overall, over the past decade, our understanding of the abundance, origin, and evolution of lunar water has improved tremendously. The recent return of new samples from the Moon by the Chinese Chang'e-5 mission – from a region that is far from the Apollo and Luna landing sites – has provided further constraints on the abundance and distribution of water in the Moon's interior (Hu et al., 2021). However, all available samples were collected from the lunar (near-) surface, and they have, therefore, all been affected by cosmic ray spallation reactions (e.g., Curran et al., 2020). Thus, as outlined above, the CRE age of the targeted samples and the cosmogenic D production rate (P_D) must be known to correct measured D/H ratios for the cosmogenic contribution. The CRE age of lunar samples can be estimated by comparing the accumulated abundances of cosmogenic noble gas nuclides ($^3\text{He}_{\text{cosm}}$, $^{21}\text{Ne}_{\text{cosm}}$, $^{38}\text{Ar}_{\text{cosm}}$) with their respective production rates (in atoms $\text{gram}^{-1} \text{year}^{-1}$ or an equivalent unit), which themselves are controlled by the chemical conditions and the shielding conditions. The most prominent issue of this method is that published empirical or theoretical production rates of cosmogenic noble gas nuclides are highly variable, even when variations in chemistry are taken into account (Bogard et al., 1971; Hohenberg et al., 1978; Leya et al., 2001; Reedy, 1981). Consequently, for any given lunar sample, a significant range of CRE ages can be obtained from the accumulated nuclide method (Füre et al., 2021b). To improve our understanding of the exposure history of lunar samples, new calibration points from 'young' geological units, which simple exposure histories, are crucially needed. Therefore, it is noteworthy that young volcanic features (so-called 'irregular mare patches') have recently been identified on the Moon which appear to have been emplaced within the last 100 Ma (Braden et al., 2014; Qiao et al., 2020). Although the

relatively recent formation ages and emplacement mechanisms of these features are debated (e.g., Qiao et al., 2020, and references therein), a sample return from these sites might not only provide key insights into the composition of the lunar mantle and the thermal evolution of the Moon, but it would also permit both the absolute radiometric *and* CRE age of a given sample to be determined. In this way, new empirical noble gas (He, Ne, Ar, Kr, Xe) production rates could be obtained which would then form the basis for improved physical models for cosmogenic nuclide production over time in extraterrestrial materials.

The use of nitrogen isotopes as tracers of the origin of lunar volatiles is challenging because Apollo samples are stored and handled at the NASA Johnson Space Center in glove cabinets that are purged with high-purity N₂ gas to minimize degradation of the samples (Füre et al., 2015b). To circumvent the issue of terrestrial contamination, the nitrogen content of lunar magmas could potentially be investigated through *in situ* SIMS analyses of MIs trapped in phenocrysts of mare basalts. Olivine-hosted MIs, with various textures and compositions, are common in mare basalts, particularly in those collected during the Apollo 12 mission (e.g., Roedder and Weiblen, 1972), and they have already been targeted for analyses of water concentrations and hydrogen isotope ratios by SIMS (Ni et al., 2019; Singer et al., 2017; Stephant et al., 2020). For two previous studies (Füre et al., 2020, 2017), I obtained eight Apollo 12 and 15 mare basalts (12004, 12009, 12018, 12020, 12075, 12076, 15016, 15535) from NASA's CAPTEM. I have already found several MIs in polished olivine grains of these Apollo samples, and I aim to locate additional MIs. The major element composition of the MIs will be determined by electron microprobe analyses, and I will then target the inclusions for nitrogen analyses by SIMS. To my knowledge, these will be the first analyses of this kind, and the results may provide key information on the nitrogen content of the lunar mantle source(s) sampled by the Apollo 12 and 15 mare basalts. Notably, if the inclusions are large enough, they could also be targeted for analyses of water abundances and hydrogen isotope ratios; this would allow me to study the coupled N–H signature of the lunar mantle source(s), and, ultimately, to gain new insights into the volatile content and isotopic signature of the lunar mantle.

8 – Outlook and future research objectives

“The more I learn, the more I realize how much I don’t know.” — Albert Einstein

Over the past decade, I have used volatile element (H, C, N, noble gases) isotopes to investigate geochemical and cosmochemical processes for terrestrial and extraterrestrial applications, with the aim of better understanding the origin(s) and evolution of volatile elements on Earth and other planetary bodies in the inner and outer solar system. However, with every new dataset that I obtained, either from a new type of sample or using a different analytical approach, numerous new questions arose – if not from myself then from curious or critical peers. My **future research objectives and priorities**, founded on the methodologies that I developed at CRPG's noble gas and SIMS facilities, are to fill (some of) these knowledge gaps. To this end, I aim to consolidate and extend my collaborations with colleagues – including senior and early-career researchers as well as students – at CRPG and at other national and international institutions. As mentioned in **Chapter 6**, I recently turned my attention to metal-rich meteorites; analyses of their H, C, N and/or noble gas content and isotopic composition by 'bulk' static noble gas mass spectrometry and *in situ* secondary ion mass spectrometry will represent a new step forward in my research. To tackle these new challenges, I submitted an **ERC Consolidator Grant proposal** ('IRONIS') in March 2022; based on novel multi-light-element isotopic analyses of irons and other Fe-Ni alloy-rich meteorites and experimental simulations, project 'IRONIS' aims to answer the fundamental questions of (i) how the distributions of H, C, and N (and their carrier phases) evolved in space and time within the earliest stages of the protoplanetary disk, and (ii) how H, C, and N were distributed between metals and silicates during planetesimal accretion, differentiation, and subsequent evolution. Ultimately, by investigating the remnants of the first planetesimal populations, project 'IRONIS' would provide new fundamental insights into the cosmochemical history and evolution of life-forming light elements in the inner and outer solar system.

In collaboration with Béatrice Luais, I aim to determine the **light element (and noble gas) content and isotopic composition of iron meteorites of different groups** whose Ge and/or Mo–Ru–W isotopic signatures have already been well characterized. Whereas it has been argued that the N isotopic compositions of iron meteorites record the NC-CC dichotomy (Rubin, 2018; Scott et al., 2018b; Grewal et al., 2021), indicating that the earliest planetesimals in the inner and outer protoplanetary disk accreted isotopically distinct N, Fe-Ni alloys of NC- and CC-type irons seem to record comparable C isotopic compositions (Deines and Wickman, 1975; Sugiura, 1998; Sugiura et al., 2000). To better assess the validity of these conclusions, I plan to determine *in situ* the N isotopic compositions of various NC- and CC-type irons by SIMS (alongside C isotopic ratios) and by static noble gas mass spectrometry (alongside noble gas abundances and isotopic ratios). *In-situ* SIMS analyses will provide new insights on the spatial distribution of N and C abundances and isotopic ratios in different Fe-Ni alloys (kamacite and taenite) in meteorites, without any contamination by

coexisting silicate inclusions and other accessory phases. Coupled N-noble gas analyses, in contrast, are key for detecting any solar gases in Fe-Ni alloys (Vogt et al., 2021) and for quantifying the contribution of cosmogenic ^{15}N in silicate-inclusion-bearing irons. Ultimately, comparison with chondrite data will provide new insights into the spatiotemporal evolution of N and C isotopic variations in the protoplanetary disk, thus improving our understanding of the N and C isotopic signatures of the planetary building blocks in the terrestrial planet-forming region. Determining the N, C, and noble gas contents and isotopic compositions of 'magmatic' iron meteorites, which represent our only available analogue for material from Earth's core, may also allow us to better trace the behavior of these elements during planetary formation and differentiation.

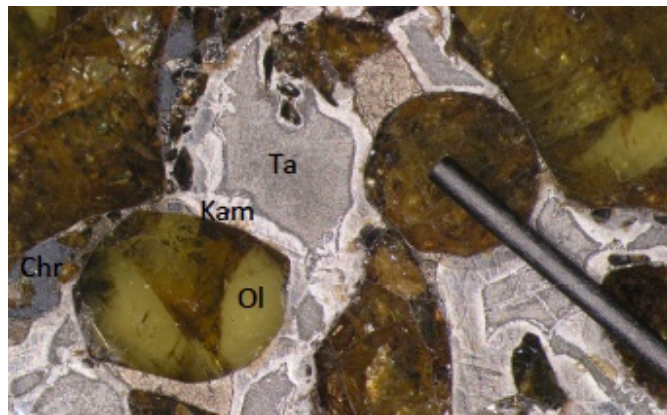


Figure 8.1. Microscope image of the Main Group pallasite 'Brahin'. Both well-rounded and angular olivine crystals (Ol) are dispersed within Fe-Ni alloy (Kam, Kamacite; Ta, taenite). Small amounts of chromite (Chr) are present. Image credit: B. Luais.

In addition to iron meteorites, pallasites may provide further insights into the N isotope variations of planetary bodies formed during the first stages of the protoplanetary disk. In collaboration with Julie Gamblin, who will work at CRPG as an assistant engineer for one year (01 Oct 2022 – 31 Sept 2023), we aim to complete our **nitrogen isotope investigation of pallasites** (see also **Section 1.2.** of this manuscript). For this project, I requested financial support from the National Program of Planetology (PNP, CNRS-INSU) in September 2022. Pallasites ('stony-irons', predominantly composed of olivine embedded in Fe-Ni alloy; **Figure 8.1.**) have long been thought to originate from the core-mantle boundaries of differentiated planetesimals; updated metallographic cooling rates and chemical compositions, however, indicate an impact origin for these objects (Yang et al., 2010, 2007; Walte et al., 2020). Importantly, $\epsilon^{54}\text{Cr}$, $\epsilon^{50}\text{Ti}$, and $\Delta^{17}\text{O}$ isotopic systematics imply that the parent body of the 'Eagle Station' (ES) pallasites formed in the CC reservoir, whereas the 'Main Group' (MG) pallasites are derived from a body accreted in the NC reservoir (Dey et al., 2019; Scott et al., 2018a; Shukolyukov and Lugmair, 2001; Warren, 2011). The MG pallasites have further been linked to the NC-type IIIAB irons based on the trace element compositions of alloys and the O isotopic compositions of silicates (Clayton and Mayeda, 1996; Scott, 1977; Wasson and Choi, 2003). To assess these genetic relationships, for the first time, based on N isotopic measurements, we have

already analyzed some alloy fragments and olivine separates by static noble gas mass spectrometry, and we plan to complete this work next year. While most samples will be heated under vacuum using a new CO₂ laser (MIR10, installed at CRPG's noble gas facility in November 2021), we will also test the all-metal induction furnace for gas extraction; although this technique is expected to result in slightly higher blanks (≤ 9 picomoles N₂ for Pt crucibles heated to 1400 °C), it will likely permit more rigorous control of temperature and, thus, better quantification of the gas released from different phases. Importantly, the coupled N-noble gas data will permit N isotope ratios in silicates to be corrected for the cosmogenic ¹⁵N contribution. The results will reveal whether the alloy and silicate phases in pallasites formed at equilibrium from a common N source. Similar or very distinct N isotopic ratios may provide additional clues to the formation mechanism of pallasites, e.g., alloy–silicate equilibration at the core-mantle interface or at shallower depths *vs.* impact-induced mixing of olivine and metal. Finally, the new N isotopic dataset will provide new insights into possible relationships between irons and different alloy-rich meteorite groups (and chondrites). If N can be used to define genetic relationships, they may confirm or refute those suggested by oxygen isotopes or trace elements.

One of my major objectives is to **develop a novel SIMS protocol for analyzing the N content and isotopic composition of iron meteorites and other Fe-Ni alloy-rich meteorites (e.g., pallasites)**. The distributions of ¹⁵N and ¹⁴N in meteoritic and synthetic Fe-Ni alloys can be investigated by targeting the CN⁻ molecular ions at mass stations 26 and 27 (**Figure 8.2.**; Dalou et al., 2019a; Sugiura, 1998; Sugiura et al., 2000a); thus, ¹²C¹⁵N⁻/¹²C¹⁴N⁻ ratios can be determined at a precision of a few permil, provided at least one calibrant with a known N isotopic composition is available. However, it is questionable if absolute N abundances can be derived from the intensity of the CN⁻ signal because the efficiency of C-N recombination reactions (and the resulting ¹²C¹⁴N⁻ ion yield) likely depends on both the C and N concentrations in the sample (Füre et al., 2018a; Regier et al., 2016). Consequently, for N concentration measurements in Fe-Ni alloys with variable C contents (e.g., 2–1000 ppm C in kamacite and taenite of various iron meteorite groups; e.g., Goldstein et al.,

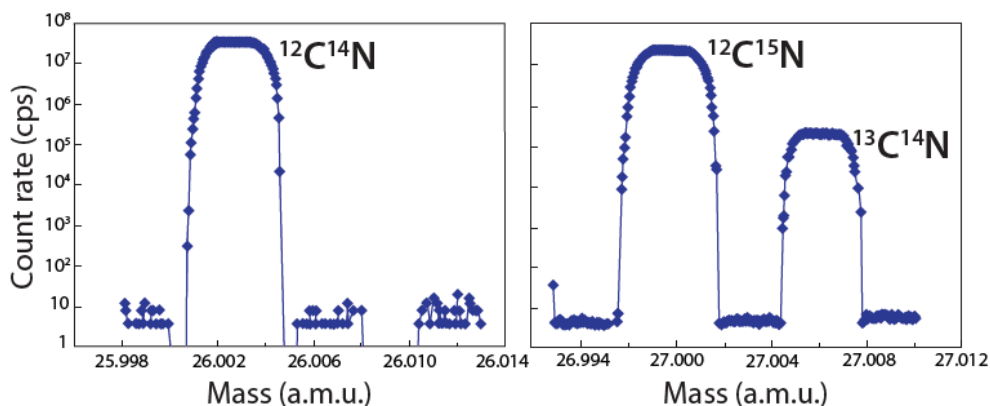


Figure 8.2. Mass spectra at mass stations 26 and 27 for a synthetic Fe-Ni alloy (containing ~2 wt% N) obtained with a mass resolution ($m/\Delta m$) of ~10,000 using the CAMECA IMS 1280 HR at CRPG. From C. Dalou (unpublished).

2017), an independent ion signal may need to be targeted. To investigate if the N contents of Fe-Ni alloys can be accurately and precisely quantified by SIMS, I aim to assess the yields and corresponding detection limits of secondary elemental or molecular N ions ($^{14}\text{N}^+$, $^{12}\text{C}^{14}\text{N}^-$, $^{56}\text{Fe}^{14}\text{N}^-$, and $^{133}\text{Cs}^{14}\text{N}^+$) sputtered from samples with known N contents. Four certified NBS stainless steel reference materials (NBS661, NBS662, NBS663, and NBS664), containing 0.003–0.0041 wt% N, are already available at CRPG, and additional steels with certified N contents will be purchased (e.g., from the collection of European Certified Reference Materials). The N contents and isotopic compositions of the standards can be cross-calibrated by static noble gas mass spectrometry at CRPG (and/or by electron microprobe analysis for samples containing ≥ 0.03 wt% N; Dalou et al., 2017). Natural alloy samples, for which N abundances can be determined by static noble gas mass spectrometry, may also serve as calibrants, provided that N is distributed homogeneously within them. Ultimately, by targeting the $^{12}\text{C}^{14}\text{N}^-$ and $^{12}\text{C}^{15}\text{N}^-$ signals together with an additional elemental or molecular N ion, I may be able to quantify the N abundances and isotopic compositions of alloys in extraterrestrial and synthetic samples using a quasi non-destructive method. The $^{32}\text{S}^-$ and $^{31}\text{P}^-$ signals could also be monitored during this mass sequence, allowing me to simultaneously determine the multi-light-element (N, C, S, P) characteristics of meteorite alloys.

In parallel to my work on metal-rich meteorites, I will also continue to investigate the nitrogen–noble gas isotopic composition of chondrites. Material that is texturally and chemically similar to the most primitive CI chondrites is contained in various howardites, eucrites, and diogenites (HEDs), ureilites, and also in ordinary and carbonaceous chondrites in the form of **xenolithic clasts**. These clasts, which are genetically unrelated to their host rocks, have the potential to provide additional important constraints on the composition and transport dynamics of volatile-rich material in the early solar system. To better assess the compositional and isotopic variability of chondritic material, I have already contributed to a multi-isotope (N, O, Ti, Cr) characterization of various clasts

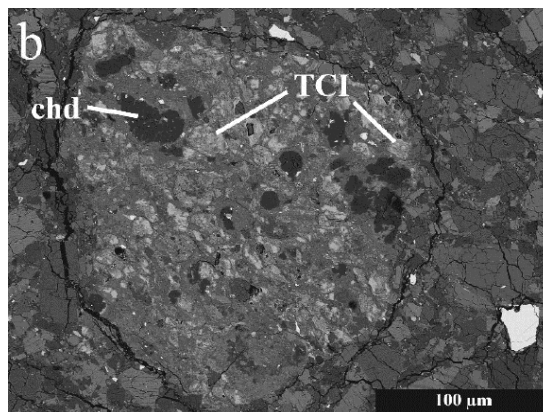


Figure 8.3. Backscattered electron image of a CM-like clast within the polymict eucrite Northwest Africa (NWA) 7542. The clast contains chondrule (chd) and mineral fragments, as well as 'lumps' of tochilinite-cronstedtite-intergrowth (TCI), which are surrounded by fine-grained rims. From Patzek et al. (2020; *in prep.*). Two clast fragments, analyzed by CO_2 laser heating and static noble gas mass spectrometry, have $\delta^{15}\text{N}$ values of $+22.3 \pm 1.2$ ‰ and $+11.8 \pm 0.9$ ‰; these values are consistent with the range of $\delta^{15}\text{N}$ values previously determined for CM chondrites ($\delta^{15}\text{N}_{\text{CM}} = -6.0$ to $+56.3$ ‰; Figure 4.2.; Alexander et al., 2012).

in HEDs, ureilites, and CR chondrites in collaboration with Markus Patzek (University of Münster) and colleagues at various other institutions (Patzek et al., *in prep.*). I determined the nitrogen (and neon, argon) content and isotopic composition of several clast fragments (between 0.024 and 0.682 mg in mass) by static noble gas mass spectrometry, and I also re-analyzed fragments of the CI chondrite Ivuna and the CM chondrite Murchison. We found that the $\delta^{15}\text{N}$ values of $\sim +100$ ‰ of clasts in ureilites and in CR chondrites fill the gap between CR and CM chondrites shown in **Figure 4.2.** Overall, the N, O, Ti, and Cr isotope results of xenolithic clasts in various groups of achondrites and chondrites demonstrate that a large diversity of primitive materials existed in the outer regions of the accretion disk. I will now further pursue this work through my participation on the **ANR project "CLASTS"**, which is led by Lydie Bonal (IPAG); the goal of this collaborative project is to combine petrographic, mineralogical, spectral, isotopic, and chronological approaches to (i) identify and determine the primary characteristics and parent body history of xenolithic clasts in a series of meteorites from the NC and CC reservoirs, (ii) characterize primordial planetesimals no longer present in the asteroid belt through the study of clasts composed of materials not sampled in the meteorite collection, and (iii) constrain the incorporation mechanism (primordial vs. subsequent accretion) and timing of clasts in their host rocks. Specifically, by determining the concentrations of cosmogenic ^3He , ^{21}Ne , and/or ^{38}Ar , and by estimating the respective production rates, we will aim to derive the irradiation history of the clasts and their host rocks. Any difference between the CRE age of the clasts and the host rocks must result from pre-exposure of the clasts to galactic cosmic rays, and may constrain the transfer time of the clasts from their primordial parent body or bodies to the final one. For this study, we will analyze the noble gas (He, Ne, Ar) and nitrogen isotopic composition of small 'bulk' fragments by CO_2 laser heating, or, alternatively, we may apply the new laser ablation extraction technique recently developed at CRPG (Byrne et al., 2021) for *in situ* analyses of specific phases. Overall, based on a detailed, multi-technique investigation of a significant number of xenolithic clasts present in various types of meteorites, project "CLASTS" will improve our knowledge and understanding of the primordial planetesimal population and of the dynamical evolution of the early solar system.

Ultimately, by combining N isotopic datasets of the solar nebular gas (Marty et al., 2011), irons and other metal-rich meteorites, as well as chondrites and their components (xenolithic clasts, chondrules, CAIs; Das and Murty, 2009; Füre et al., 2015a; Grady et al., 1986; Kung and Clayton, 1978; Murty, 1998; Russell et al., 1998), I aim to better assess the distribution and evolution of N isotopes (i.e., carried by ice and dust grains, organics, nitrides) in the protoplanetary disk through space and time. Notably, to this date, only three CAIs have been analyzed for their N isotopic compositions ($\delta^{15}\text{N}_{\text{CAI}} \approx +20 \pm 10$ ‰; Füre et al., 2015a; Murty, 1998; Russell et al., 1998). Chondrules (millimeter-sized silicate spherules that predominantly formed 1–3 Ma after CAIs; e.g., Pape et al., 2019; Villeneuve et al., 2009) record a wide range of $\delta^{15}\text{N}$ values (corrected for

cosmogenic ^{15}N) of -97 to $+164$ ‰ and -27 to $+116$ ‰ in NCs and CCs, respectively (Das and Murty, 2009). To complete existing chondrite datasets, and to better understand the N isotopic variability in chondrite components, I plan to **determine the N (and noble gas) contents and isotopic compositions of additional NC and CC chondrite fragments, CAIs, and chondrules** by static noble gas mass spectrometry. Based on this new N isotopic dataset, combined with astrophysical models and astronomical observations, I will gain new insights into the distribution and evolution of N isotopes in the protoplanetary disk and, ultimately, on the N isotopic signature of potential planetary building blocks in the terrestrial planet-forming region. Thus, the results will also improve our understanding of the origin of life-forming elements on Earth.

Based on my expertise in the analysis of small-sized extraterrestrial samples and in lunar geology, I have been selected to collaborate on several **space missions**, which will allow me to have access to new samples and datasets that will provide new insights into the formation and evolution of chondritic asteroids and on the history of the lunar regolith, respectively. I am a member of the sub-team 'Volatiles' in charge of analyzing the nitrogen–noble gas composition of gas and solid samples that were returned from the asteroid Ryugu by the **Hayabusa2** spacecraft (JAXA) in Dec 2020. I recently co-authored two articles that summarize the results obtained by several Japanese and international laboratories (Okazaki et al., *Science Advances*, *under review*; Okazaki et al., *Science*, *under review*). The nitrogen-noble gas results obtained for two grains analyzed at CRPG's noble gas facility are discussed in detail in an separate article (Broadley et al., *under review*), and, following the 2022 (first) Ryugu sample announcement of opportunity, we obtained two additional, larger Ryugu grains for further analyses by static noble gas mass spectrometry. In addition, I am a sample science collaborator on the sample science team of the **OSIRIS-REx** mission (NASA), which is expected to return samples from the asteroid Bennu in 2023. I have been selected to carry out nitrogen and noble gas measurements of individual grains at the CRPG, in collaboration with Prof. Bernard Marty, with the goal of better constraining the isotopic variability and source(s) of nitrogen in chondritic materials. Finally, I note that the **Emirates Lunar Mission** (ELM), lead by the Mohammed Bin Rashid Space Centre (MBRSC), will send a small rover ('Rashid') to the nearside of the Moon in 2022/23. I am a member of the Landing Site Selection Working Group, the Path Planning Group, and the ELM Science Operations Core Team. As such, I have contributed to characterizing the geological characteristics of the prime and back-up landing sites. I will participate on the rover operations in early 2023 at the control center in Dubai, where I will be involved in the decision-making process regarding the rover trajectory and the selection of targets for thermal and microscopic imagery.

Last but not least, I will continue to collaborate with Maxim Portnyagin (GEOMAR) on a research project that aims to provide fundamental and currently missing information on the CO_2 (and N) cycle at subduction zones on Earth. The project focuses on the accurate determination of the initial CO_2 (and N) concentration in parental magmas from three active volcanic arcs – Kuril-Kamchatka,

Central America, and Calabria – based on *in situ* analyses of volatiles in olivine-hosted melt inclusions. To reverse post-entrapment modifications of the melt inclusions (e.g., bubble nucleation during cooling and decompression), they will be completely homogenized by heating and re-hydration using state-of-the-art one-atmosphere and high-pressure experiments. This is of particular importance for CO₂ and N because the formation of a fluid bubble can substantially deplete the coexisting melt in dissolved CO₂ and N due to their low solubilities in silicate melt (e.g., Bernadou et al., 2021; Boulliung et al., 2020; Dixon et al., 1995; Libourel et al., 2003; Moore et al., 2015; Wallace, 2005). For this project, I will be in charge of determining the N content of the melt inclusions by SIMS at CRPG. The results are expected to improve our understanding of the behavior and fate of N at subduction zones. This work is also particularly important to me on a personal level, because it will allow me to further address some of the questions that I had started to investigate during my PhD at SIO with Dave Hilton, who passed away in 2018.

Overall, in the future, I hope to be able to focus primarily on fundamental, curiosity-driven research, and to actively participate in analyzing samples and developing new methodologies in the laboratory. Whereas my PhD was focused on generating massive datasets using well-established analytical techniques, I have come to realize that I particularly enjoy "fiddling" with mass spectrometers for challenging, non-routine sample analyses. The dynamic and stimulating scientific and technological environment at CRPG is crucial for this approach, and the funding agencies will hopefully continue to support high-risk research in geo- and cosmochemistry that will contribute towards better understanding the origin and evolution of volatile elements on planetary bodies in the inner solar system.

*“Science, my lad, is made up of mistakes,
but they are mistakes which it is useful to make, because they lead little by little to the truth.”*
— Jules Verne, *A Journey to the Center of the Earth*

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