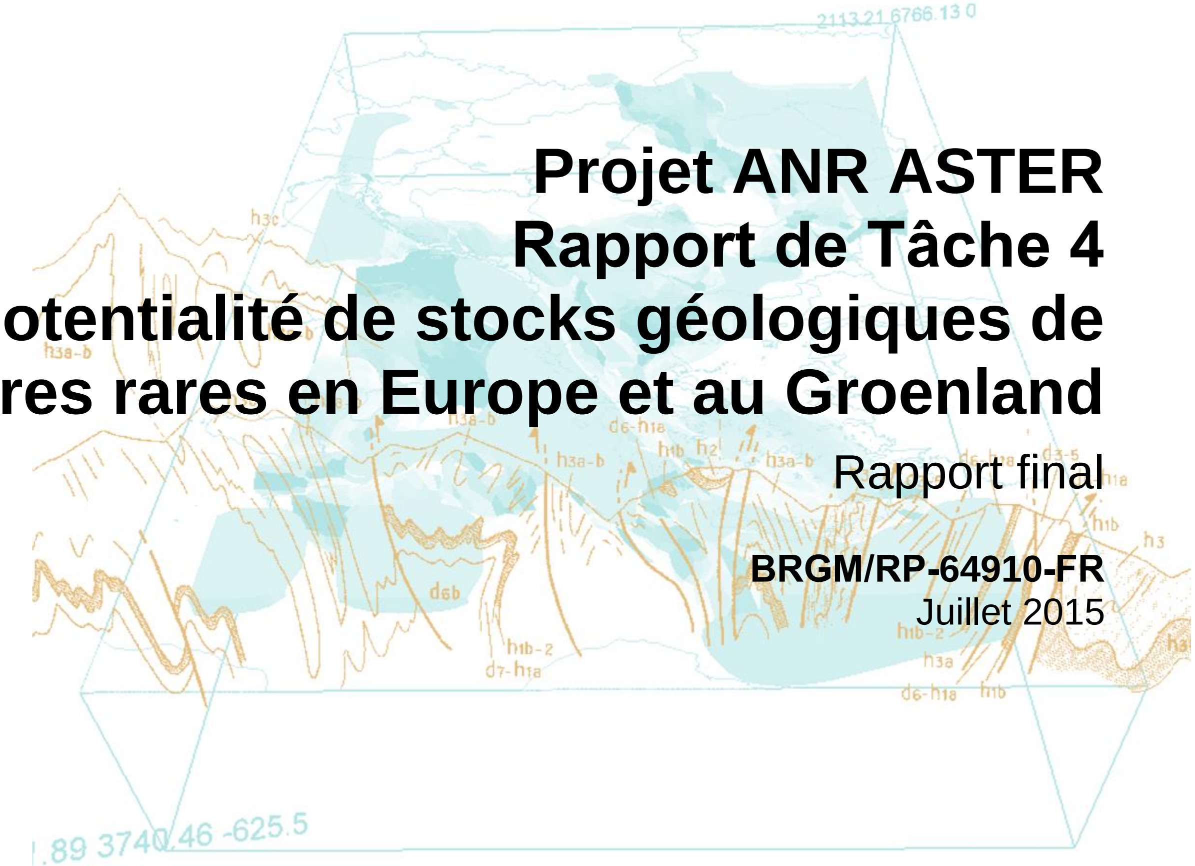

Projet ANR ASTER
Rapport de Tâche 4
Potentialité de stocks géologiques de terres rares en Europe et au Groenland

Rapport final

BRGM/RP-64910-FR
Juillet 2015

Projet financé par l'ANR - Project funded by the ANR

Document public

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Juillet 2015

Étude réalisée dans le cadre du projet
ANR-11- ECOT-002

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Synthèse

Le projet ASTER se place dans un contexte de risques de sécurité d'approvisionnement de certaines terres rares, essentielles pour des écotechnologies énergétiques comme les lampes basse-consommation, les éoliennes, les batteries pour véhicules hybrides et électriques, etc. Il s'agît dans ASTER de réaliser une analyse des flux de matière (MFA) pour dresser une cartographie des flux et stocks de ces terres rares dans l'UE des 28. Parmi les caractères novateurs du projet on citera en particulier :

- la prise en compte de stocks lithosphériques ; c'est-à-dire de potentialités géologiques, où le champ d'investigation a été élargi à l'Europe continentale afin d'inclure la totalité du bouclier scandinave, l'Ukraine et la Turquie, ainsi que le Groenland.

Deux des principaux objectifs du projet sont :

i. le développement de diagrammes dits « Sankey », qui permettent de visualiser graphiquement les flux / stocks des terres rares sélectionnées dans l'UE-28 et notamment de mieux identifier la provenance des flux de matière première amonts issus de la production minière ainsi que les potentialités de recyclage. Tandis que les tâches 3 et 6 ont été dédiées à la collecte des informations et à la réalisation de cette méthodologie ;

ii. la tâche 4, objet du présent rapport, identifie les domaines géologiques à fort potentiel en gîtes de terres rares et apporte une évaluation des ressources en terres rares contenues dans le sous-sol européen.

Les résultats sont présentés sous la forme de cartes gîtologiques et de graphiques permettant notamment :

- d'identifier les domaines géologiques les plus fertiles ;
- d'identifier le potentiel géologique en terres rares de l'EU-28 ;
- d'évaluer les ressources en terres rares du sous-sol européen.

L'objectif final du projet ASTER est d'avoir une vision plus réaliste de la « criticité » de certaines terres rares, et notamment les terres rares lourdes, pour l'UE-28.

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1. Introduction

1.1. DÉFINITIONS

Le glossaire ci-dessous donne la définition de certains termes utilisés dans le rapport et les annexes.

- **occurrence** : concentration naturelle ou secondaire de terres rares correspondant à l'une des trois définitions suivantes :
    - **gisement de terres rares** : concentration naturelle ou secondaire économiquement exploitable,
    - **prospect** : concentration généralement naturelle de terres rares dont l'existence est connue grâce à des observations de terrain et étayées par des petits travaux miniers (sondages, tranchées, …) mais dont l'intérêt économique reste à démontrer,
    - **gîte** : désigne une concentration naturelle significative de terres rares sans connotation économique,
    - **indice** : est une indication de la présence de minéralisation de terres rares et dont l'existence est uniquement reconnue par des observations de terrain. Ce terme sert à indiquer la présence d'une minéralisation sans certitude économique ou une concentration sans aucun intérêt économique.
- **minerai** : désigne une roche ou un résidu de l'activité anthropique contenant une concentration d'un ou plusieurs minéraux de terres rares et en quantité suffisante pour être économiquement exploitable ;
- **primaire** : ce qualificatif, appliqué à une substance, indique que la production est issue d'un minerai non recyclé ;
- **secondaire** : ce qualificatif, appliqué à une substance d'origine anthropique, indique que sa production est issue du recyclage de déchets ;
- **minéralisation** : désigne une concentration naturelle locale de minéraux de terres rares. Dans les gisements la minéralisation désigne la partie exploitable et économique ;
- **potentiel géologique** : correspond à la fertilité en terres rares d'une région ou d'un pays. Il s'agit d'une première estimation généralement qualitative basée sur des critères géologiques ;
- **ressource minière** : il s'agit d'une minéralisation dont l'enveloppe et le volume ont fait l'objet d'une première approximation, bien qu'incertaine, à l'aide de sondages, tranchées, galeries de reconnaissance… ;
- **réserve minière** : partie(s) de la ressource ayant fait l'objet de travaux plus poussés et dont l'exploitabilité technologique et économique a été démontrée lors d'une étude de faisabilité.

1.2. LES TERRES RARES

Les terres rares sont des éléments dits « en traces » dans la plupart des environnements naturels. Elles constituent un groupe exceptionnel de 17 éléments chimiques métalliques, cohérents en termes de rayon ionique, de charge et de coordination (figure 1). Elles comprennent, selon les définitions (e.g. Henderson, 1984; Lipin et Mckay 1989; Jones *et al*., 1996, Atwood 2012), les lanthanides (de ^{57}La à ^{71}Lu), l'yttrium (^{39}Y) et parfois le scandium (^{21}Sc).

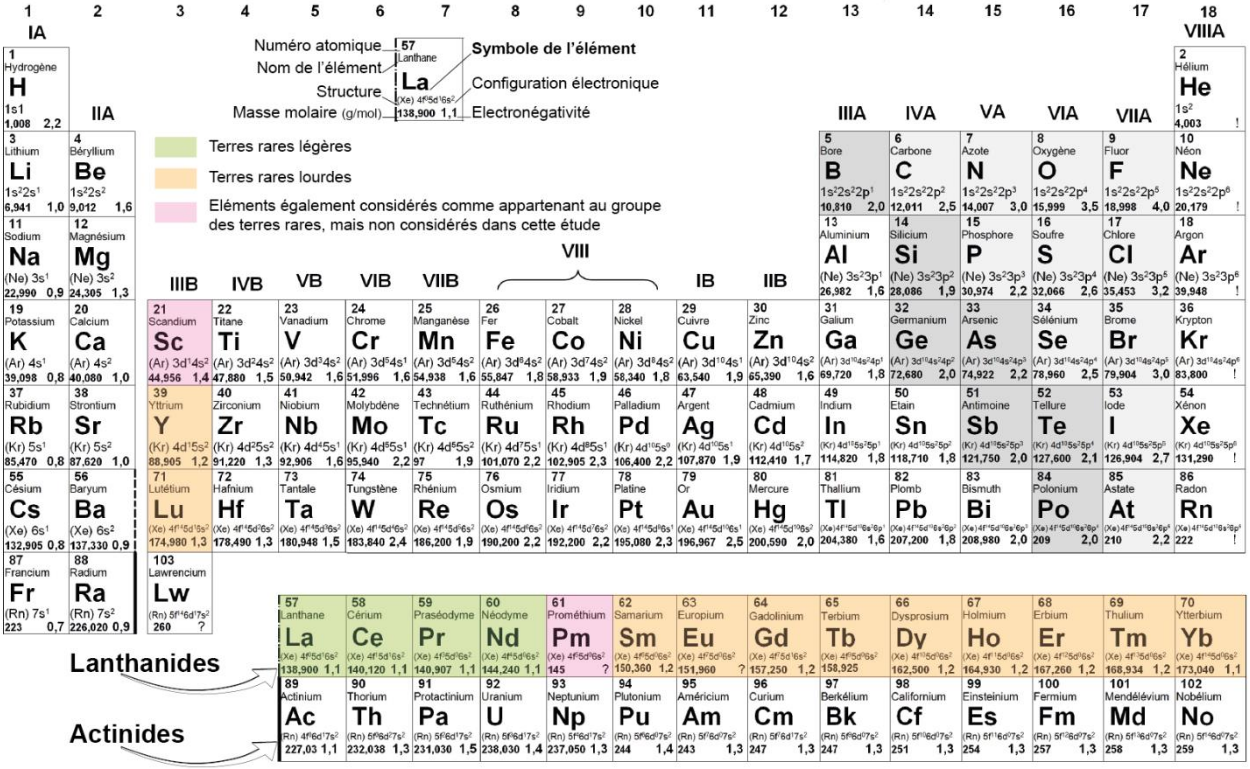

Figure 1 - Les différentes terres rares replacées dans la classification périodique des éléments.

Toutefois l'appartenance du Sc à ce groupe reste matière à débat car son comportement dans les environnements géologiques est généralement différent de celui des autres terres rares. De même, le prométhium (^{61}Pm) ayant une demi-vie extrêmement courte, il est inexistant dans la nature.

Par conséquent, nous considérerons dans ce rapport seulement 15 éléments comprenant 14 lanthanides plus l'yttrium que nous assimilerons au groupe des terres rares (REE – de l'anglais Rare Earth Elements).

Selon les configurations spécifiques des électrons au sein de chaque atome, les terres rares peuvent être divisées en deux sous-groupes. On distingue ainsi le sous-groupe des terres rares légères et celui des terres rares lourdes. L'appartenance de certaines terres rares à l'un des deux sous-groupes est encore fortement discutée (e.g. Gupta et Krishnamurthy 2005 ; Chakhmouradian et Wall 2012 ; McLennan et Taylor 2012 ; Weng *et al.*, 2013 ; Zepf 2013).

Dans le cadre du projet ASTER, une classification propre à l'industrie minière a été suivi (Weng *et al.*, 2013) aux dépens de celle préconisée par l'union internationale de chimie pure et appliquée (IUPAC). En effet, pour des raisons économiques liées à l'abondance géologique, aux coûts du traitement de minerai, aux techniques de séparation, etc., de nombreux acteurs de l'industrie minérale considèrent comme terres rares légères : La-Ce-Pr-Nd (LREE de l'anglais Light Rare Earth Elements), et comme terres rares lourdes : Sm-Eu-Gd-Tb-Dy-Ho-Er-Tm-Yb-Lu-Y (HREE de l'anglais Heavy Rare Earth Elements).

Comme ces mêmes acteurs industriels séparent et vendent leurs concentrés de terres rares sous forme d'oxydes, il est d'usage de considérer ces éléments en termes d'oxydes de terres rares (REO Rare Earth Oxides). Ainsi, les termes oxydes de terres rares légères (LREO pour Light Rare Earth Oxides) et oxydes de terres rares lourdes (HREO pour Heavy Rare Earth Oxides) sont généralement considérés au cours de toutes la chaine de valeur allant de l'exploration minière, en passant par l'extraction minière jusqu'à leur séparation.

Sur un plan économique, le marché des terres rares est aujourd'hui dominé par la Chine, dont la part dans la production mondiale est supérieure à 85 % (2013-2014). Par conséquent, la consommation de terres rares dans l'UE-28 dépend massivement des importations chinoises (figure 1a), ce qui soulève l'importante question de la vulnérabilité de l'approvisionnement.

En effet, les terres rares sont chimiquement cohérentes et se caractérisent par une gamme de propriétés électroniques, magnétiques, optiques et catalytiques exceptionnelles et particulièrement importantes pour le développement et la pérennisation de certaines technologies vertes émergentes (tableau 1).

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Other
Aimants permanents			16.1	64.5				3.2	16.1		
Batteries NiMH	52.5	31.0	4.0	11.0						1.5	
Alliage	25.4	53.1	5.5	16.0							
Catalyse automobile	4.8	90.4	2.0	2.9							
Catalyse pétrolière	89.6	10.4									
Poudres de polissage	30.5	66.0	3.5								
Verres spéciaux	23.4	67.3	1.0	2.9						2.1	3.3
Luminophores	10.3	7.9				6.1		4.0		71.6	
Céramiques	16.2	12.0	5.9	11.4						54.6	
Autres	18.4	39.5	4.0	14.4	1.9		0.9			20.9	

Tableau 1 - Proportions relatives (%) de terres rares utilisées dans différentes applications industrielles (Guyonnet et al., *2015).*

Ainsi, le marché des terres rares est devenu particulièrement tendu, lorsque les prix de ces différents métaux ont fortement augmenté en 2011 en raison des quotas plus stricts sur les exportations chinoises engagées en 2010 (figures 2b, c, d), et d'une demande croissante en ce qui concerne les véhicules hybrides ou électriques, les éoliennes et les lampes fluorescentes compactes. En conséquence, en Juillet 2011, les prix du Dy et du Tb ont dépassé les prix moyens de la période 2004-2009 par des facteurs de l'ordre 30 et 10 respectivement (figure 2d). Depuis, les prix des terres rares sont revenus à des niveaux plus soutenables (figures 2c, d.) et ce en raison de divers facteurs incluant dans un premier temps l'éclatement d'une bulle spéculative et dans une moindre mesure : la diversification de la production minière (e.g. Mount Weld en Australie entrée en production en Août 2011 et Mountain Pass aux États-Unis), le développement du recyclage (Binnemans *et al.,* 2013) et l'optimisation et / ou la substitution de certaines terres rares dans les produits (par exemple des aimants permanents en Dy ; Yan *et al.,* 2010).

En novembre 2013, le Centre commun de recherche de la Commission européenne a publié un rapport sur les métaux essentiels et leur importance pour une décarbonisation du secteur énergétique de l'UE (Moss *et al.,* 2013). Parmi les huit métaux considérés comme « très critiques », six étaient des terres rares: praséodyme (^{59}Pr), le néodyme (^{60}Nd), l'europium (^{63}Eu), le terbium (^{65}Tb), le dysprosium (^{66}Dy) et l'yttrium (^{39}Y).

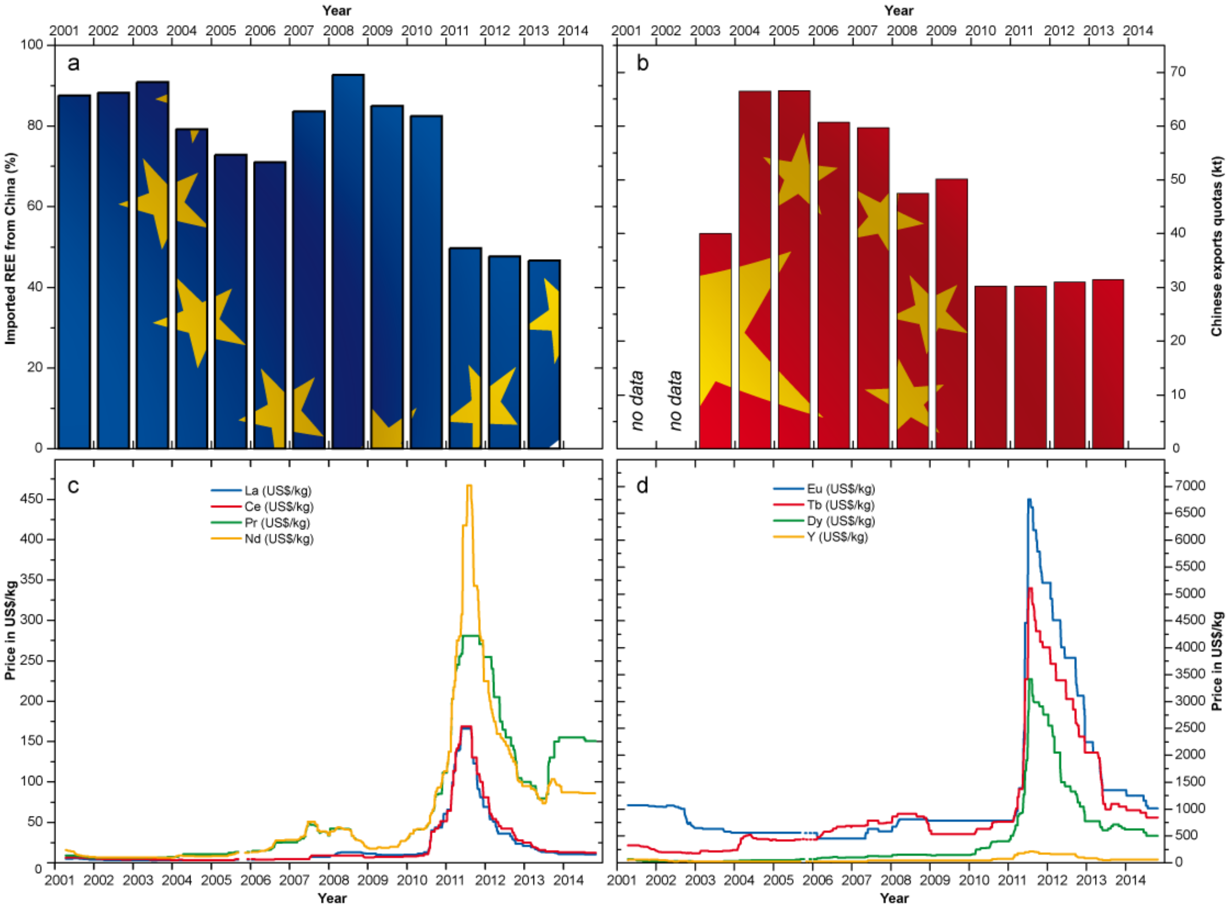

Figure 2 - Économie des terres rares. (a) importations de terres rares dans UE-28 depuis la Chine entre 2001 et 2012 (données EUROSTAT). (b) Quotas d'exportation chinois d'oxydes de terres rares entre 2003 et 2013. En 2010, les exportations chinoises de terres rares ont été limitées à 30 259 tonnes d'oxydes de terres rares. Prix (fob) des (c) terres rares légères (La, Ce, Pr, Nd) et (d) de certaines terres rares lourdes (Eu, Tb, Dy, Y) entre Janvier 2000 and décembre 2014 (données metal-pages).

La criticité est une notion qui combine l'importance d'un élément pour le développement d'une technologie avec le risque de rupture de l'approvisionnement dans les secteurs stratégiques de l'économie. Afin d'atténuer le risque de pénurie de l'offre, l'EU-28 encourage les États membres à développer et à diversifier leurs sources d'approvisionnement, qu'elles soient primaires (minières) ou secondaires grâce à la réutilisation, au recyclage et la réduction des déchets. Ainsi, de nombreuses industries sont à la recherche de moyens afin de diversifier leurs sources d'approvisionnement en terres rares, en particulier compte tenu de leur importance pour une large gamme de nouvelles technologies vertes telles que des aimants permanents, les batteries rechargeables NiMH, les luminophores pour lampes basse consommation, catalyseurs, etc.

Sur le plan géologique, la notion de criticité est d'abord liée à l'abondance naturelle de ces éléments dans la croûte terrestre. En effet, les terres rares ne sont pas rares. Leur abondance naturelle dans les roches de la croûte terrestre est au moins équivalente à celle des métaux de base (Zn, Cu, Pb, Ni, Co) et donc bien moins rares que des métaux précieux comme l'argent ou l'or (figure 3). En revanche, les LREE (ou LREO), étant les plus abondantes en masse, elles se retrouvent donc à des concentrations parmi les plus élevées dans de nombreux gisements primaires (Jones *et al.,* 1996). À l'inverse, les HREE (HREO) sont nettement moins abondantes à l'instar des métaux rares (Sn, W, Ta). Elles sont donc bien plus rares (excepté pour l'Y) y compris dans les gisements. Pour cette raison, les HREE sont considérées comme étant bien plus critiques que les LREE, d'où leur valeur marchande bien plus élevée que celle des LREE (figures 2c, d). Par conséquent, le rapport HREO / LREO est un paramètre critique à prendre en considération pour l'évaluation du potentiel d'un gisement.

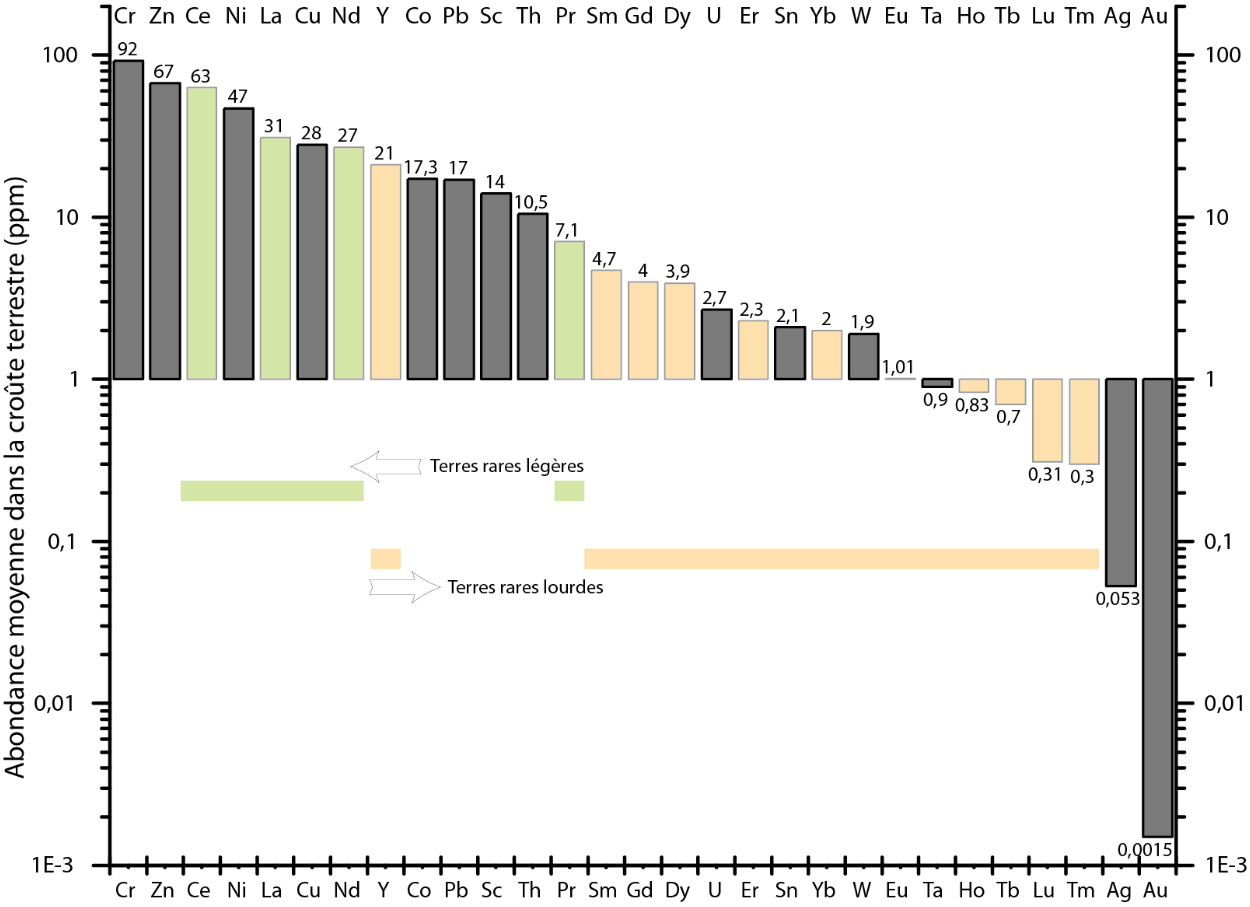

Figure 3 - Abondance naturelle des terres rares et d'autres éléments dans la croûte terrestre (ppm, d'après Rudnick et Gao, 2003).

Par conséquent, les projets d'exploration minière de terres rares situés en Europe et à son voisinage peuvent fournir d'excellentes alternatives aux importations chinoises massives en Europe. Dans un tel contexte, ce présent rapport propose une évaluation des ressources primaires en terres rares contenues dans la lithosphère européenne. Les limites du système considèrent ainsi les frontières géologiques de l'Europe dite continentale ainsi que l'ensemble du Groenland dépendant du Danemark.

Cette étude repose sur une meilleure compréhension des processus de formation des gisements de terres rares, en tenant compte de la grande diversité des gîtes et de leurs paramètres géologiques associés mais aussi du potentiel de recyclage secondaire à partir de déchets miniers.

En premier examen, une carte inédite représentant la distribution d'un peu plus de 410 occurrences de terres rares, classées par typologie en Europe et au Groenland, est proposée (Figure 7). Une telle synthèse géologique ouvre la voie pour le ciblage des zones d'exploration de terres rares parmi les plus prometteuses.

2. Méthodologie

2.1. LIMITES DU SYSTÈME ÉTUDIÉ

Les limites du système considéré dans cette étude sont liées à deux paramètres : économiques et géologiques. En effet, si les paramètres économiques nécessitent d'inclure dans cette étude tous les pays de l'UE-28 en y incluant le Groenland les paramètres géologiques quant à eux servent à fermer le système notamment à l'est en respectant les frontières dites géologiques.

Ainsi, les frontières orientales du système étudié comprennent l'ensemble du bouclier scandinave y compris la péninsule de Kola en Russie, ainsi que l'Ukraine et la Turquie.

Par conséquent, sont également inclus dans cette étude, les potentiels candidats à l'Union Européenne tels que l'Albanie, la Macédoine, le Monténégro, le Kosovo, la Serbie et la Turquie, mais également les pays du continent européen non membre de l'UE (e.g. Suisse, Norvège, Bosnie-Herzégovine) mais nouant des liens étroits avec l'UE-28.

L'intégration de la Russie dans cette étude est liée au fait qu'il existe bien une production de terres rares en Europe continentale bien que située dans la péninsule de Kola et dont au moins 50 % de cette production est exportée dans l'UE-28 en Estonie où les terres rares sont transformées par Molycorp (env. 2500t/an REO, MetalResearch 2013).

2.2. SOURCE DES DONNÉES

La collecte des données nécessaires à l'évaluation du potentiel en terres rares de l'Europe et du Groenland a été réalisée par le BRGM. Les données sont issues de :

- cartes géologiques et minières, et rapports publiés par les services géologiques nationaux ;
- communiqués de presse et rapports produits par des sociétés minières ;
- articles scientifiques ;
- bases de données minières comme ProMine (promine.gtk.fi) et FODD (en.gtk.fi/informationservices/databases/fodd/).

Enfin la base de données géochimiques FOREGS (FORum of European Geological Surveys) a été utilisée à l'échelle de la France afin de mieux comprendre la distribution des terres rares dans les eaux de surface. Le programme FOREGS a consisté en un échantillonnage des eaux à une maille régulière sur l'Europe. En France, 119 échantillons ont été prélevés dans les eaux de surface de bassins-versants <100 km².

2.3. DIFFICULTÉS RENCONTRÉES

Le projet ASTER ayant été initialement destiné à la France, la redéfinition très en amont des contours du système étudié à l'échelle de l'UE-28, nous a conduit à modifier la méthodologie initiale afin de s'adapter au contexte géologique européen plus diversifié, et, à prendre en considération le caractère imprécis et non harmonisé de l'information disponible.

En janvier 2013, le projet européen « EURARE » (« European Rare Earths »), co-financé par la Commission européenne a été lancé. Il vise à développer un schéma de développement durable de l'exploitation de gisements de terres rares européens. De nombreux partenaires issus de plusieurs pays européens prennent part au travail, dont le BRGM. Parmi les tâches de ce projet, une synthèse des gisements de terres rares européens est prévue, recouvrant ainsi une partie des objectifs du projet ASTER. Afin d'éviter une concurrence entre les deux projets, des partenariats ont été noués afin d'avancer ensemble et de coopérer sur l'échange de données. Ainsi, la base de données ASTER a été utilisée pour compléter la base de données en cours de construction d'EURARE, et des publications scientifiques communes sont en cours de rédaction. Le projet ASTER a ainsi pu être présenté au groupe de travail EURARE, avec un accueil très positif de la part de la communauté scientifique du projet européen.

2.4. LIVRABLES

✓ Typologie et potentiel des gisements de terres rares

Le travail consiste à établir une base de données des gisements et occurrences. Le livrable de cette sous-tâche est une base de données de modèles de gisements avec l'ensemble des critères qui permettent de les explorer.

✓ Compréhension des processus de minéralisation

Il s'agit de caractériser les modèles de gisements afin de mieux comprendre le rôle des différents processus géologiques dans la genèse des minéralisations de terres rares. Les travaux prévus dans cette tâche feront l'objet de publications et communications scientifiques. Ces travaux sont essentiels et conduisent à porter un jugement d'expert sur la potentialité des stocks géologiques de terres rares en Europe.

✓ Évaluation du potentiel en terres rares du continent européen

L'ensemble des données acquises précédemment a permis d'aborder le cœur de la problématique de cette tâche, à savoir de délimiter des « zones potentielles » où il existerait des gisements à découvrir et de proposer une première estimation du potentiel européen.

Le travail ainsi présenté vise à alimenter l'analyse des flux de matières (MFA) afin d'estimer les flux et stocks de certaines terres rares à l'échelle de l'UE-28, en tenant compte des potentialités géologiques.

3. Typologie des gisements de terres rares

3.1. MINÉRALOGIE DES TERRES RARES

Le terme « rare » est souvent considéré comme un abus de langage, car comme nous venons de le voir (Figure 3), ces éléments sont, finalement, assez fréquents dans la croûte terrestre. Les minéraux renfermant des terres rares peuvent ainsi se rencontrer dans un large éventail de conditions géologiques depuis la croûte profonde et le manteau jusqu'aux conditions de surface soumises aux processus d'altération tout en y incluant les processus hydrothermaux.

En fait, c'est la faible quantité de minéraux porteurs de terres rares observables dans la nature qui justifie le terme « rare », (Figure 4a). On notera que cette faible quantité est liée, *pro parte,* à des lacunes épistémiques, c'est-à-dire, à la difficulté d'analyser les terres rares avec précision dans certains minéraux mais également à l'absence de mesure dans de nombreuses études minéralogiques.

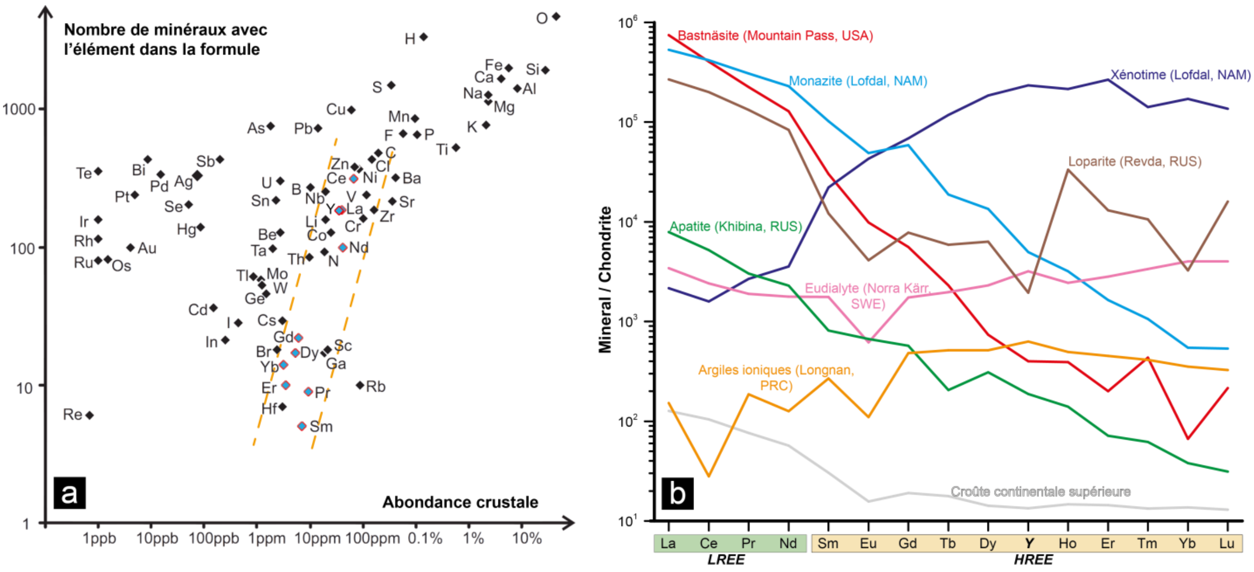

Figure 4 - (a) Nombre de minéraux comportant un élément specifique, dont les terres rares, dans sa formule strucutrale (Higgins et Smith, 2010).(b) Profils de terres rares d'une sélection des principaux minéraux exploités ainsi que de l'eudialyte qui pourrait dans un futur proche devenir un nouveau minerai de terres rares. Ces données sont comparées à l'abondance moyenne des REE dans la croûte continentale supérieure (Castor, 2008 ; Wall et al.*, 2008 ; Schilling* et al.*, 2011 ; Henderson, 1984 ; Chi et Tian, 2008 ; McDonough et Sun, 1995). (Pour le chimisme des phases, se reporter au Tableau 2)*

Bien que près de 200 espèces minérales de terres rares soient aujourd'hui connues (ce qui reste faible), seules quelques-unes d'entre elles présentent un intérêt commercial. En effet, si les REE sont fréquemment incorporées dans le réseau cristallin de différents types de minéraux tels que les carbonates, les oxydes, les silicates ou encore les phosphates en substitution d'autres éléments chimiques plus courants, l'industrie minérale d'hier et d'aujourd'hui n'a cherché à valoriser qu'un très faible nombre de minerais de terres rares (Tableau 2) : à savoir la bastnäsite (fluorocarbonate), la monazite (phosphate), le xénotime (phosphate), et la loparite (oxyde). Dans le passé, les terres rares ont également été extraites de l'apatite en Russie et en Afrique du Sud, mais cette production fut extrêmement limitée (Gupta et Krishnamurthy, 2005). Dans les années 1990-2000, la compagnie Norsk Hydro a récupéré les terres rares contenues dans les apatites russes de la péninsule de

Kola dans leur unité de Glomfjord en Norvège. Ces terres rares ont par la suite été séparées en France à la Rochelle par Rhodia (2007-2009). Excepté le xénotime qui peut être considérablement enrichi en HREE et dans une moindre mesure l'eudialyte, tous ces minéraux sont essentiellement caractérisés par leur grande richesse en LREE (Figure 4b). Les technologies liées au traitement de ces minerais de terres rares sont aujourd'hui bien établies (Jordens *et al.*, 2013). En ce qui concerne les volumes de production minière, la bastnäsite est le principal minerai de terres rares. Elle est extraite des principales mines chinoises de Bayan Obo, Weishan et Maoniuoing ainsi qu'à Mountain Pass aux États-Unis.

Depuis les années 1970, les argiles dites ioniques ou argiles latéritiques d'ion-adsorption, constituent une importante source de HREE (Bao et Zhao, 2008). Cette production, uniquement localisée dans le sud de la Chine (provinces de Jiangxy, Guangdong, et Guangxi) est favorisée par un coût de main d'œuvre bas, et des procédés d'extraction relativement simple par lixiviation *in situ* avec des solutions neutres ou acides (Wall, 2014). Cependant, avec des teneurs de minerai extrêmement faible, de tels procédés questionnent sur l'équilibre entre faisabilité économique et protection de l'environnement. Néanmoins, la forte proportion de HREE couplée à la très faible concentration en éléments radioactifs (U, Th) associés à ce type de gisement, en font un défi attrayant dans l'exploration minérale.

Mineral name	**Chemical formula**	**Weight percent**		
		RE_2O_3	**ThO_2**	**UO_2**
Yttrofluorite	$(Ca_{1-x}[HREE]_x)F_{2+x}$	15.5	-	-
Fluocerite	$[LREE]F_3$	83	-	-
Euxenite	$([REE],U,Th)(Nb,Ta,Ti)_2O_6$	16-30	<4.3	3-9
Fergusonite	$[REE]NbO_4$	43-52	<8	<13.6
Loparite	**$(Na,[LREE],Ca,Sr,Th)(Ti,Nb,Ta)O_3$**	**28-37**	**1.6**	**0.03**
Pyrochlore	$(Ca,Na,U,[REE])_2(Nb,Ta)_2O_6(OH,F)$	< 22	<4.4	<27
Uraninite	UO_2	<1.5	<12.2	50-98
Ancylite	$Sr[LREE](CO_3)_2(OH).H_2O$	46-53	<0.4	<0.1
Bastnäsite	**$[LREE]CO_3(F,OH)$ ☝**	**58-75**	**<2.8**	**<0.1**
Parisite	**$Ca[LREE]_2(CO_3)_3F_2$ ☝**	**50-59**	**<4**	**<0.3**
Synchysite	**$Ca[LREE](CO_3)_2(F,OH)$ ☝**	**48-53**	**<5**	**-**
Allanite	$([REE],Ca)_2(Al,Fe)_3Si_3O_{12}(OH)$	2.5-17	<3.2	0.017
Clay minerals	**e.g. adsorbed REE on kaolinite / halloysite $Al_2Si_2O_5(OH)_4$**	**<<4**	**<0.01**	**<0.001**
Eudialyte	$(Na,[REE])_{15}(Ca,[REE])_6(Fe,Mn)_3(Si,Nb)_2(Zr,Ti)_3Si_{24}O_{72}(OH,F,Cl,H_2O)_6$	1-10		<0.1
Gadolinite	$[REE]_2FeBe_2Si_2O_{10}$	45-54	<0.4	
Steenstrupine	$Na_{14}[LREE]_6Mn_2Fe_2(Zr,Th)(PO_4)_7Si_{12}O_{36}.3(H_2O)$	< 31	<6.2	<1
Thorite	$(Th,U,[REE])SiO_4$	<3	65-81	10-16
Zircon	$(Zr,[HREE],Th,U)SiO_4$	< 19	0.01-0.8	0.01-4
Apatite	**$Ca_5(PO_4)_3(F,Cl,OH)$**	**<<2***		**<0.05**
Monazite	**$([LREE],Th,Ca)(P,Si)O_4$**	**35-71**	**<20**	**<16**
Xenotime	**$([HREE],Zr,U)(P,Si)O_4$**	**54-74**	**<8.4**	**<5.8**

Tableau 2 - Chimie des principaux minéraux de terres rares rencontrés dans la nature. En gras, sont mentionnés les minéraux valorisés par l'industrie extractive, à la date de publication du présent rapport. (☝ phases minéralogiques pouvant être - de façon exceptionnelle - enrichies en HREE. Dans ce cas, ces minéraux ont fait l'objet d'une exploitation minière à Kutessay au Kirghizistan.

Parce que les lanthanides partagent de nombreuses similitudes avec les éléments du groupe des actinides (Figure 1), les minéraux de terres rares renfermeront quasi-systématiquement des éléments radioactifs tels que le thorium et/ou l'uranium (Tableau 2). L'uraninite et la thorite pourront également accompagner ces minéraux de terres rares. La présence de ces éléments radioactifs constitue ainsi un frein au développement des projets miniers. En effet, la radioactivité va suivre toutes les étapes du processus d'enrichissement des minerais jusqu'aux procédés métallurgiques. Ces minéraux et éléments radioactifs constituent ainsi un déchet qui devra être rigoureusement géré. Pour ces raisons, il est essentiel de s'intéresser aux teneurs en U et Th dans les gisements mais plus particulièrement aux rapports ThO_2/REO et U_3O_8/REO des minéraux constituant le minerai. En outre, les terres rares devraient être plus souvent considérées comme de potentiels sous-produits de l'extraction de l'uranium. Par exemple, dans les années 1980, les mines d'uranium d'Elliot Lake au Canada ont produit un concentré à 60 à 70 % REO à partir de la lixiviation d'un stérile d'uranium (Gupta et Krishnamurthy 2005). Dans de nombreux cas, les terres rares pourraient être récupérées à partir de résidus miniers (par exemple Olympic Dam en Australie) ou en tant que co-produits de U (ex. projet de Kvanefjeld au Groenland). Il est à noter qu'en mai 2011, la société Areva a signé un protocole d'entente avec Solvay-Rhodia, pour développer des procédés d'enrichissement pour les gisements contenant un mélange d'uranium et de terres rares.

Enfin, ces dix dernières années ont vu l'émergence d'un important marché de l'exploration des terres rares dont l'un des objectifs était la définition de ressources en dehors de la Chine. Si différents projets sont ainsi en cours de valorisation de par le monde, nombre d'entre eux constituent des projets innovants car non-conventionnels. Certains projets correspondent à de nouveaux modèles de gisements, d'autres cherchent à valoriser de nouveaux types de minéraux tels que le pyrochlore ou la fergusonite, des oxydes, et de nombreux silicates telles que l'allanite, l'eudialyte, ou la steenstrupine. Ces phases minérales, notamment celles silicatées, présentent l'avantage d'être enrichies en HREO en comparaison des carbonates de terres rares par exemple (Figure 4b). Une compilation des données sur la composition de ces minéraux est présentée dans le Tableau 2.

Ainsi, de nombreux projets de recherche s'intéressent à la séparation et à l'enrichissement de ces nouvelles catégories de minerais dits « non-traditionnels » car ces phases minérales notamment celles silicatées ont tendance à être davantage enrichies en HREO que les carbonates par exemple (Figure 4b).

3.2. GÎTOLOGIE DES TERRES RARES

Les gisements de terres rares peuvent être divisés en deux grandes catégories (Figure 5) : **i**) les gisements primaires ou endogènes associés aux processus magmatiques et hydrothermaux et **ii**) les gisements secondaires ou exogènes où les enrichissements sont liés à des processus sédimentaires et/ou climatiques (Walters *et al.,* 2011 ; Chakhmouradian et Wall, 2012).

Malgré une grande variété de modèles de gisements, seuls cinq d'entre eux sont aujourd'hui exploités pour leur contenu en terres rares : les carbonatites, les gîtes du magmatisme hyperalcalin (ou peralcalin), les placers, les gîtes à argiles ioniques et enfin les gîtes latéritiques comme ceux développés sur les carbonatites (ex. Mount Weld en Australie). Tous les autres modèles de gisements proposés en figure 5 correspondent à des occurrences dites non conventionnelles bien qu'explorées. Les caractéristiques de ces cinq grands types sont présentées ci-dessous et résumées dans la Figure 6.

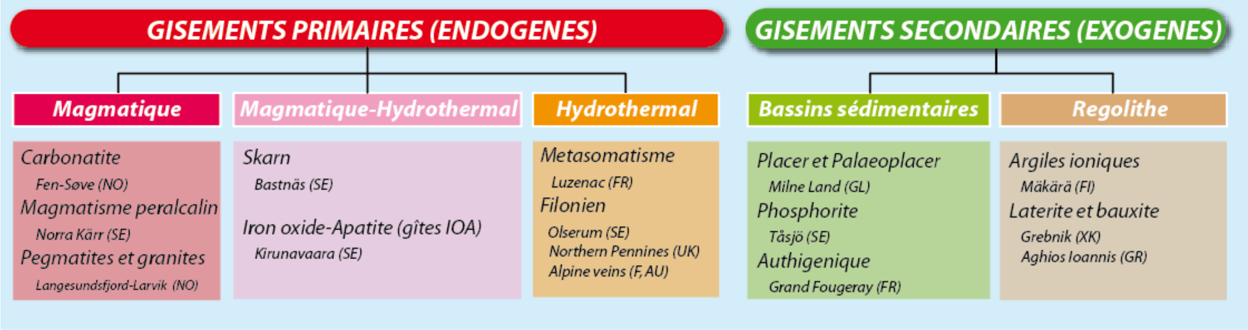

Figure 5 - Classification des gîtes et gisements de terres rares. Pour chacun des modèles distingués, un exemple de gîte ou gisement européen a été proposé.

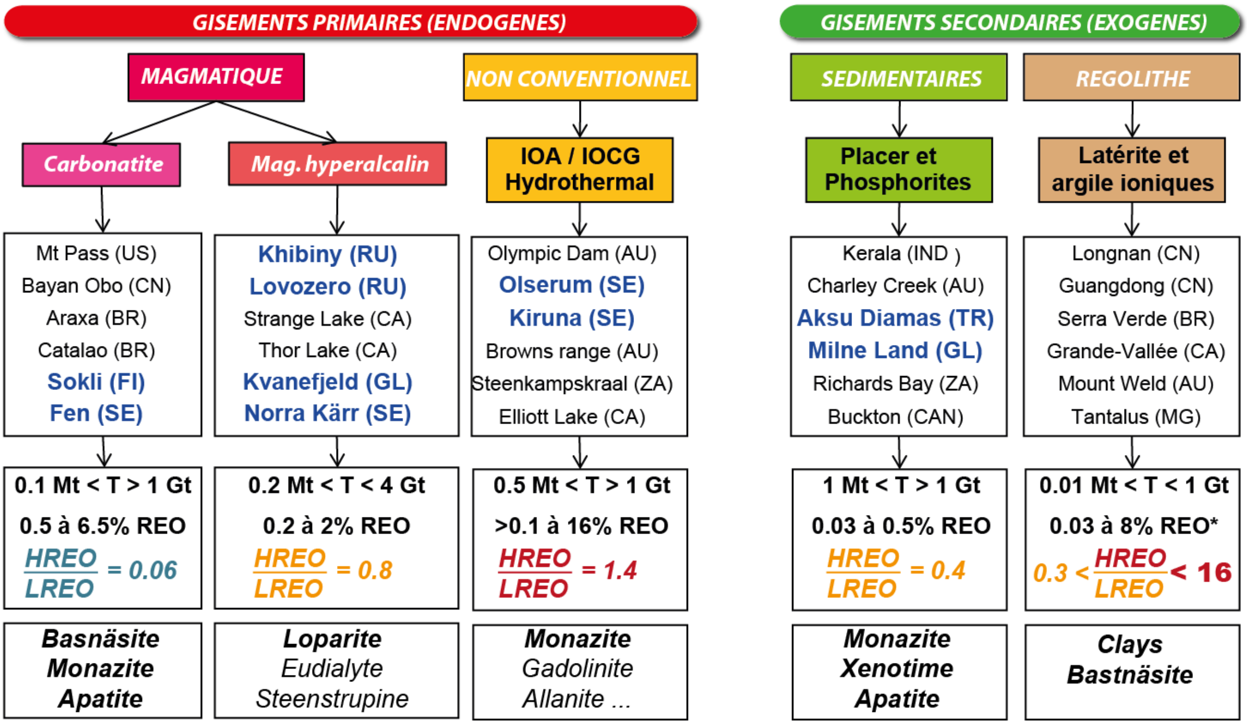

*Figure 6 - Caractéristiques des principaux modèles de gisements. **En bleu**, les gîtes de classe mondiale localisés en Europe ou au Groenland.T : tonnage, * la valeur de 8 % correspond au gisement de Mount Weld, le rapport HREO/LREO correspondant est de 0,3.*

3.2.1. Les gîtes primaires ou endogènes

Ces types de gisements représentent, depuis le milieu des années 1960, l'essentiel de la production de terres rares. Cette dernière provient pour l’essentiel de roches ignées alcalines dites de type A rencontrées en contexte de rifting. Il s’agit d’un type de magmatisme sous-saturé en SiO_2 par rapport à Na_2O, K_2O, et CaO (Winter, 2001). On distingue deux importants types de roches alcalines : les carbonatites et les roches hyperalcalines :

- les carbonatites sont des roches presque exclusivement composées de carbonates et dont la proportion modale de calcite, dolomite et/ou ankérite doit être supérieure à 50 %. Par conséquent, leur teneur en SiO_2 sera, par définition, inférieure à 20 %. Dans les carbonatites, les teneurs en REO sont généralement supérieures à 1 % avec des teneurs pouvant, exceptionnellement, dépasser 5 % comme à Bayan Obo en Chine ou Mountain Pass aux États-Unis. L'enrichissement en terres rares est surtout marqué par les LREE portées par les phases suivantes : bastnäsite, monazite, apatite et allanite (Gupta et Krishnamurthy, 2005). Le ratio HREO/LREO est faible est généralement inférieure à 0,1. En 2014, près de 60 % de la production mondiale de terres rares étaient issus de carbonatites (*e.g.* Bayan Obo, Mountain Pass et Mount Weld) ;

- les roches hyperalcalines sont définies par un rapport molaire$(Na_2O + K_2O)/Al_2O_3 > 1$. Ces roches généralement plutoniques ont tendance à être spatialement associées à des carbonatites. Les teneurs en terres rares associées à ce type de gisement sont plus faibles que dans les carbonatites et généralement inférieures à 2 %. (e.g. Norra Kärr en Suède et Kringlerne au Groenland titrent à 0,6 % REO). Une spécificité de ce type de gisement est d'être fréquemment enrichi en HREE (par comparaison avec les carbonatites). Ainsi le ratio HREO/LREO, bien que très variable est généralement supérieur à 0,15 et parfois même bien supérieur à 1. Les principaux minéraux utiles sont la loparite, l'eudialyte, la gadolinite ou encore la steenstrupine. Ils sont souvent associés à des noms de roches « exotiques » tels que les ijolites, lujavrites, kakortokites, urtites ou melteigites. Seuls les gisements russes à loparite de la péninsule de Kola sont aujourd'hui exploités pour leurs terres rares. Ils ne représentent que 2 % de la production mondiale. De nombreuses compagnies minières s'intéressent aujourd'hui à ces types de gisements localisés au Canada, au Groenland ou encore en Suède. Dans ces exemples, la principale phase minérale porteuse de terres rares est un silicate complexe de Nb, Zr et REE nommé eudialyte. Des compagnies minières comme Tasman Metals développent des techniques brevetées pour extraire les terres rares de ce minéral.

En sus de ces deux grandes familles de gisements, il convient de rajouter les champs de pegmatites, associées aux intrusions magmatiques saturées ou sous-saturées de type A (rarement de type I), qui peuvent contenir des quantités significatives de terres rares légères, portées par l'allanite ou la monazite ou de terres rares lourdes (gadolinite).

En outre, des concentrations notables de REE ont également été observées dans des gisements dits « non conventionnels » d'affiliation magmatique-hydrothermal comme les gisements à oxydes de fer, cuivre et or (IOCG) ou à magnétite-apatite (IOA) du district de Kiruna dans le nord de la Suède (Harlov et al., 2002). Là, les REE sont associées à l'apatite ou à l'allanite. Il est également intéressant de mentionner la présence de terres rares associées à des processus métasomatiques et à des paléo-systèmes hydrothermaux, tels que les minéralisations filoniennes à fluorine-barytine, ou encore les gîtes uranifères. L'intérêt porté par les compagnies minières pour les gisements hydrothermaux est lié à leur richesse en HREE.

3.2.2. Les gîtes secondaires ou exogènes

Les gisements secondaires représentaient la majeure partie de la production de REE avant les années 1970, en particulier par l'exploitation de placers à monazite (Orris et Grauch, 2002). Les gisements de type placer sont toujours exploités mais ne représentaient plus que 3 % de la production mondiale en 2014. En revanche, un nouveau modèle de gisement de type argiles latéritiques d'ion-adsorption est aujourd'hui activement exploité en Chine du sud-est (Province de Guangdong et Jiangxi) et depuis plusieurs décennies. Ce type de gisement suscite à présent l'attention d'investisseurs occidentaux (*e.g.* prospects de Grande Vallée au Canada, Serra Verde au Brésil, ou encore du Projet Tantalus à Madagascar). Aujourd'hui près de 30 % de la production minière mondiale de terres rares est issue de ce type de gisement.

Il convient donc de distinguer deux types de gîtes secondaires : les gisements associés aux processus de surface et appartenant au régolithe et les gisements de bassins associés aux environnements sédimentaires.

- on pourra ainsi observer dans des bassins sédimentaires, des gîtes de type placer correspondent à des accumulations de minéraux lourds dans des sables et graviers séparés par des processus de gravité lors de leur transport par l'eau ou le vent. Les processus diagénétiques consolideront ces placers les transformant en paléoplacers. Les placers sont généralement récents, d'âge Tertiaire ou Quaternaire, même si quelques-uns sont datés du Précambrien. Les principaux minéraux de terres rares sont la monazite, le xénotime, la fergusonite, l'euxenite et l'allanite (Donnot *et al*., 1973;. Morteani 1991; Mohanty *et al.,* 2003; Elsner 2007). Un autre processus d'accumulation cette fois-ci de micro-organismes et d'algues mais en contexte marin pourra produire sous l'action de la diagenèse des concentrations de phosphates appelés phosphorites. Ces roches constituées exclusivement d'apatite peuvent dans certains contextes renfermer des REE ainsi que de l'uranium. Enfin, concernant les gîtes authigéniques, la diagenèse de certaines roches silico-clastiques enrichies en matière organique pourra dans certains cas, sous l'élévation de la température, produire des concentrations notables en REE (Tuduri *et al.,* 2013).

- les processus de surface vont provoquer par réactions d'hydrolyse et d'oxydation, d'hydratation, voire de décarbonatation une altération chimique des roches et minéraux en complément des phénomènes physiques. Ainsi, les éléments solubles (Mg, Ca) sont lessivés en partie, parfois en totalité sous des climats très agressifs. Les parties insolubles (Fe, Al, une partie des REE) restent sur place pour se recombiner en minéraux de néoformation, principalement des argiles, des hydro-phosphates ou des carbonates.

  Ainsi en contexte latéritique, l'altération de roches initialement riches en REE (e.g. carbonatite) pourra produire des gisements secondaires de terres rares encore plus riches. C'est le cas du gisement latéritique de terres rares de Mount Weld en Australie développé aux dépens d'une carbonatite et dont la teneur d'exploitation est aujourd'hui supérieure à 8 % (Lottermoser, 1990). Localement les teneurs en REE peuvent dépasser 30 % (Olivier *et al.,* 2015). Le cas des gîtes d'argiles ioniques est souvent associé à l'altération de granites. Dans ce contexte les terres rares peu solubles sont adsorbées à la surface d'argiles néoformées (halloysite / kaolinite). Ces gisements nombreux mais de très petites tailles (quelques dizaines de milliers de tonnes) sont exploités malgré leur (très) faible teneur (de 0,03 à 0,35 % REO, Chi et Tian, 2008).

4. Caractérisation du potentiel géologique en terres rares de l'Europe et du Groenland

Les données présentées dans cette partie ont fait et feront l'objet de communications et rédactions d'articles de rang A.

Communications :

Tuduri, J., Charles, N., Guyonnet, D., Pourret, O., Rollat, A., Escalon, V. and Planchon, M., 2014. Rare Earth Elements in Europe and Greenland: A synthesis of lithospheric and anthropospheric potentials, 24ème Réunion des Sciences de la Terre, Pau, France, pp. 368.

Charles, N., Tuduri, J., Guyonnet, D., Pourret, O. and Melleton, J., 2014. Rare Earth Elements in Europe and Greenland: A novel synthesis of occurrences, 1st Conference on European Rare Earth Resources, Milos Island, Greece, pp. 39-40.

Articles :

Charles, N., Tuduri, J., Guyonnet, D., Melleton, J. and Pourret, O., 2013. Rare earth elements in Europe and Greenland: a geological potential? An overview. In: E.e.a. Jonsson (Editor), Proceedings of the 12th Biennial SGA Meeting, Uppsala, Sweden, pp. 1698-1701.

Goodenough, K.M., Schilling, J., Jonsson, E., Charles, N., Kalvig, P., Deady, E.A., Sadeghi, M., Tuduri, J., Schiellerup, H., Müller, A., Bertrand, G., Arvaniditis, N., Shaw, R.A., Thrane, K., Keulen, N.. Europe's rare earth element resources: metallogenetic provinces and geodynamic setting. Soumis @ Ore Geology Reviews.

Charles, N., Tuduri, J., Goodenough, K., Melleton, J., Pourret, O., Bailly, L., Guyonnet, D., Kolb, J., Borst, A., Bartels, A. and Kokfelt, T., F, (en cours de rédaction). Geology and rare earth elements potential in Europe and Greenland. A soumettre @ Ore Geology Reviews.

Les occurrences de terres rares de l'Europe et du Groenland sont également divisées en deux grandes catégories : les gisements primaires et les gisements secondaires. La figure 7 présente la distribution des différentes occurrences de terres rares, c'est-à-dire 412, compilées dans le cadre du projet ASTER et localisées en Europe et au Groenland. Si les gisements affiliés au processus endogènes sont principalement localisés dans le nord de l'Europe et au Groenland, on pourra constater que tous ceux liés à des processus d'altération de type latérite-bauxite sont systématiquement localisés au sud de l'arc Alpin (Figure 7).

Dans le détail, les formations géologiques localisées dans les domaines Paléoprotérozoïque et Paléozoïque portent les 2/3 des occurrences recensées (Figure 8a). On notera également que les occurrences les plus fréquentes sont celles de type placers et paléoplacers (Figure 8b). Les occurrences des domaines d'âge Paléozoïque et plus particulièrement varisques portent l'essentiel des gîtes de types placers-paléoplacers, soit 61 % d'entre eux (Figure 8c). Ces derniers constituent principalement des indices bien que certains aient été des cibles d'exploration notamment en France dans les années 1970 (e.g. minéralisations du Grand Fougeray en Bretagne ou de Bailleul en Normandie) et donc évaluées. Excepté Bailleul qui reste un petit gisement avec 3,5Mt @ 0,5 %REO (soit 15kt REO), tous constituent des cibles de très petites tailles dont le potentiel et l'intérêt économique sont limités. La figure 8d représentant quant à elle le nombre d'occurrences en fonction du pays, montre que près de 20 % des occurrences de terres rares sont situées en France. Ce chiffre ne signifie en aucun cas que la France possède un fort potentiel géologique mais que ce pays comme d'autres (e.g. Belgique) ont mis en place dans le passé d'importants programmes d'inventaires miniers. Les principales occurrences françaises sont des gisements authigéniques à monazite et leur produit d'érosion des placers, nombreux, à monazites dites grises. Ainsi le véritable potentiel en terres rares de l'Europe comme du Groenland est uniquement situé dans des domaines géologiques anciens, dits cratoniques d'âge Archéen ou Paléoprotézoïque des boucliers Baltique et du Groenland. Les principaux types de gisements associés sont d'affiliation magmatique. On distingue les carbonatites,les complexes peralcalins ainsi que de nombreux champs de pegmatites.

Les parties suivantes présentent la géologie et la distribution de différentes occurrences de terres rares en Europe puis au Groenland. Le Tableau 3, présente les caractéristiques et propriétés de ces différents types d'occurrences.

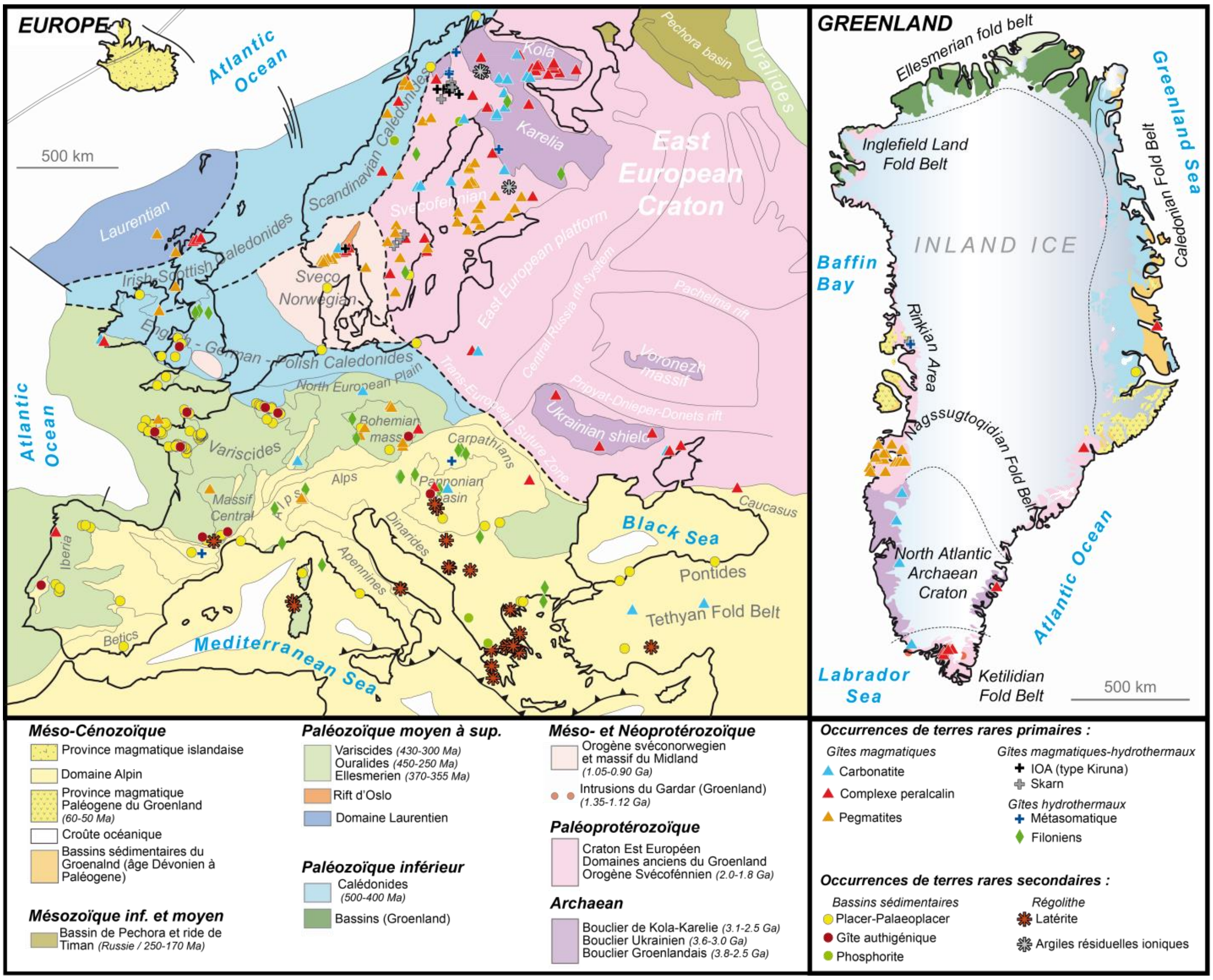

Figure 7 - Distribution des différentes occurrences primaires (endogènes) et secondaires (exogènes) de terres rares en Europe et au Groenland.

4.1. LES GÎTES DE TERRES RARES EN EUROPE

4.1.1. Les gîtes primaires

Les complexes peralcalins et les carbonatites représentent l'essentiel des occurrences de terres rares associées aux gisements primaires. Ils sont situés en Europe du Nord dans le vaste bouclier Baltique incluant la péninsule de Kola en Russie. Ce domaine dit cratonique constitue la principale zone à fort potentiel géologique.

Les intrusions peralcalines y constituent de nouveaux projets pour l'exploration minière des terres rares en Europe et dont le potentiel est avéré. Le gîte de Norra Kär en Suède correspond à une intrusion de syénite néphélinique. Le dernier rapport de pré-faisabilité montre que les ressources + réserves du gisement sont évaluées à près de 55 Mt pour une teneur moyenne de 0,55 % REO (Short *at al.,* 2015). Il s'agit du premier gisement situé dans l'EU-28 à certifier des réserves. D'autres gîtes également liés à des intrusions alcalines montrent un fort potentiel : Särna et Almunge en Suède ; Suhuvaara en Finlande et Saeterasen en Norvège. En outre, les complexes peralcalins de Khibina et Lovozero dans la péninsule de Kola renferment des « monstres » bien connus avec des réserves estimées à plus de 2 Gt @ 0,6 % REO (Sørensen, 1997 ; Arzamastsev *et al.,* 2006 ; Kogarko *et al.,* 1995 ; Orris et Grauch, 2002).

Type de gîte			Exemple d’occurrences et statut	Substances	Minéralogie des terres rares	Considerations économiques			
						REO	HREO/ ΣREO	ThO_2	UO_2
Gisements primaires (endogènes)	**Magmatic system association**	**Carbonatite**	Kovdor (RU) Active mine	**P, Fe, Zr,** Nb, Ti, REE	Apatite, pyrochlore …	916 Mt @ 0.48%	-	-	-
			Afrikanda (RU) Project	Ti, V, Fe, Nb, Ta, Th, REE,	Perovskite, pyrochlore …	627 Mt @ 0.78%	-	0.045%	-
			Fen-Søve (NO) Project	Nb, Ta, Fe, Be, Li, Sc, REE, Th, U	Apatite, bastnasite, monazite, parasite, pyrochlore, synchysite …	400 Mt @ 0.9%	2.5%	0.1%	-
			Sokli (FI) Project	P, Fe, Nb, REE, U, Ta, Zr	Apatite-(U), pyrochlore, rhabdophane	250 Mt @ 0.5%	-	-	0.01%
			Kizilcaören (TR) Project	F, Ba, REE	Bastnäsite	4.7 Mt @ 2.78%	-	0.2%	-
			Storkwitz (DE) Project	REE, Nb	Apatite, bastnäsite,	4.44 Mt @ 0.45%	3.54%	-	-
			Korsnas (FI) Closed mine	Pb, REE	Allanite, apatite, bastnasite, monazite …	0.87 Mt @ 0.97%	-	0.05%	-
		Magmatisme alkcalin-et peralcaline	Kringlerne (GL) Project	Zr, REE, Nb, Ta, Hf, Au, Cu, Zn, feldspar	Eudialyte …	4300 Mt @ 0.65%	31.6%	-	-
			Koashvinskoe (RU) Active mine	**P, nepheline**, REE	Apatite, loparite, eudialyte …	937 Mt @ 0.48%	-	-	-
			Kvanejfeld (GL) Project	U, REE, Zn, Nb	Steenstrupine, eudyalite …	619 Mt @ 1.05%	-	-	0.02%
			Umbozero (RU) Closed mine	**Nb, Ta, Ti, REE**	Apatite, loparite, eudialyte …	406 Mt @ 1.23%	-	-	-
			Norra Kärr (SE) Project	REE, Zr, Hf, Pb, feldspar	Eudialyte catapleiite …	58.1 Mt @ 0.59%	50.1%	-	0.03%
			Misvaerdal (NO) Project	P, REE	Allanite, apatite	30 Mt @ 0.07%	21.2%	0.01%	-
			Sæteråsen (NO) Project	Zr, Nb, REE	Apatite, euxenite, fergusonite, pyrochlore, zircon …	8 Mt 0.53%	18%	0.05%	-
		Pegmatite	Gloserheia (NO) Project	REE, U, Th	Allanite, apatite, euxenite, monazite, uraninite, thorite, xenotime, zircon …	4Mt @ 0.02%	-	-	-
			Tysfjord (NO) Project	Fe, REE	Allanite, zircon	100 Mt @ 0.13%	-	-	-
			Ytterby (SE) Closed mine	**Feldspar**, REE	Allanite, apatite, bastnasite, fergusonite, gadolinite, monazite, xenotime, zircon …	-	-	-	-

Tableau 3 - Caractéristiques et considérations économiques des principaux types de gîtes de terres rares en Europe et au Groenland.

Type de gîte			Exemple d'occurrences et statut	Substances	Minéralogie des terres rares	Considerations économiques			
						REO	HREO/ ΣREO	ThO_2	UO_2
Gisements primaires (endogènes)	**Systemes magmatique-hydrothermaux**	**ÎOA**	Kiirunavaara (SE) Active mine	**Fe, P, Mn**, REE	Apatite, magnetite, hematite	1943 Mt @ 0.004%	42.7%	0.003%	0.0002%
			Malmberget (SE) Active mine	**Fe, P, Mn**, REE	Apatite, magnetite, hematite	1039 Mt @ 0.01%	24.4%	-	-
			Kodal (NO) Project	Fe, P, REE, Mn, Ti	Apatite	48.9 Mt @ 0.124%	17.1%	0.003%	-
		Skarn	St Sahavaara (SE) Project	Fe, P, Mn, Cu, REE	Apatite, magnetite	121.5 Mt @ -	-	-	-
			Bastnas (SE) Closed mine	**Fe, Cu, REE**	Allanite, bastnasite …	4500 t Ce produced between 1875-1888	-	-	-
			Kallak (SE) Project	Fe, REE	Apatite, magnetite	189 Mt @ -	-	-	-
	Systèmes hydrothermaux	**Filons et et gîtes métasomatiques**	Olserum (SE) Project	REE	Allanite, apatite, monazite, xenotime …	7.8 Mt @ 0.62%	24.7%	-	-
			Lipchagskoe (RU). Project	REE, Nb	Fergusonite, perovskite, zircon …	53 Mt @ 0.12%	-	-	-
			Niaqornakavsak (GL) Project	REE	Allanite, bastnasite, fergusonite, monazite	26 Mt @ 1.36%	13.1%	-	-
			Katajakangas (FI) Project	REE, Nb, Zr, U	Allanite, fergusonite	0.46 Mt 2.81%	-	0.12%	0.025%
			Biggejav'ri (NO) Project	Sc, REE, U	Bastnasite, monazite, xenotime	0.05 Mt @ 0.2%	-	1%	-
			Northern Pennines (GB) Closed mine	**F, Ba, Pb, Zn**, REE	Monazite, synchysite, xenotime	-	-	-	-
			Luzenac (FR) Active mine	**Talc**, REE	Allanite, bastnasite, gadolinite, monazite, parsisite, synchysite, xenotime …		-	-	-

Tableau 3 - Suite.

Type de gîte			Exemple d'occurrences et statut	Substances	Minéralogie des terres rares	Considerations économiques			
						REO	HREO/ ΣREO	ThO_2	UO_2
Gisements secondaires (exogènes)	**Sédimentaires**	**Placer**	Nea Peramos (GR) Project	REE, Ti, Zr, U	Allanite, apatite, monazite, uraninite, zircon …	5.7 Mt @ 1.17%	-	0.16%	0.005%
			Plavna (RS) Showing	REE, Ti, Zr	Monazite, zircon …	-	-	-	-
			Espiguette (FR) Showing	REE	Florencite, monazite, xenotime, zircon	-	-	-	-
		Palaeoplacer	Aksu Diamas (TR) Project	Zr, Ti, Fe, REE, Sc, Nb, U, Th	Allanite, apatite, chevkinite, sphene, titanite, thorite, uranothorite …	493 Mt @ 0.067%	4.9%	0.005%	0.001%
			Milne Land (GL) Project	Zr, REE, Ti, U	Monazite, zircon …	5 Mt @ 1 %	-	-	-
			Bailleul (FR) Old project	Zr, Ti, REE	Monazite, zircon …	3.5 Mt @ 0.5%	-	0.03%	-
			Aron (FR) Old project	REE	Grey monazite	0.9 Mt @ 0.09%	5.5%	0.001%	0.0001%
		Phospho-rite	Tåsjö (SE) Project	U, REE, P	Apatite	112.5 Mt @ 0.18%	-	-	0.07%
			Pålänge (SE) Occurrence	U, REE, P	Apatite	6 Mt @ 0.004%	56.7%	-	0.03%
			Delvinaki (GR) Occurrence	REE	Apatite, organic matter	-	-	-	-
		Authi-genic	Grand Fougeray (FR) Occurrence	REE	Grey monazite	- Mt @ 0.1%	12.9%	-	-
			Rozstání (CZ) Occurrence	REE	Grey monazite	-	4.6%	-	-
			Cévennes (FR) Occurrence	REE	Apatite, monazite	- Mt @ 0.6%	-	-	-
	Régolithe	**Bauxite / Laterite**	Aghios Ioannis (GR) Active mine	**Fe, Al**, REE	Bastnasite	- Mt @ 0.02%	-	-	-
			Nazda-Vlasenica (BA) Active mine	**Al**, REE	Bastnasite, goyazite	- Mt @ 0.12%	-	-	-
			Steni Arahovis (GR) Active mine	**Al**, REE	Bastnasite, churchite, florencite, rhabdophane, xenotime, zircon…	-	-	-	-
			Nurra (IT) Active mine	**Al, Fe,** REE	Kaolinite, REE-Fe oxy-hydroxides	-	-	-	-
			Grebnik (XK) Active mine	**Al, Ni**, REE	Bastnasite, REE-Fe oxy-hydroxides, synchysite	- Mt @ 0.15%	-	-	-
		Argiles ioniques	Mäkärä (FI) ?	Kaolinite, REE	Kaolinite, monazite, rhabdophane, xenotime	-	-	-	-
			Vaulo (FI) ?	Kaolinite, REE	Kaolinite, monazite, rhabdophane, xenotime	-	-	-	-
			Virtasalmi (FI) ?	Kaolinite, REE	Kaolinite	-	-	-	-

Tableau 3 - Suite.

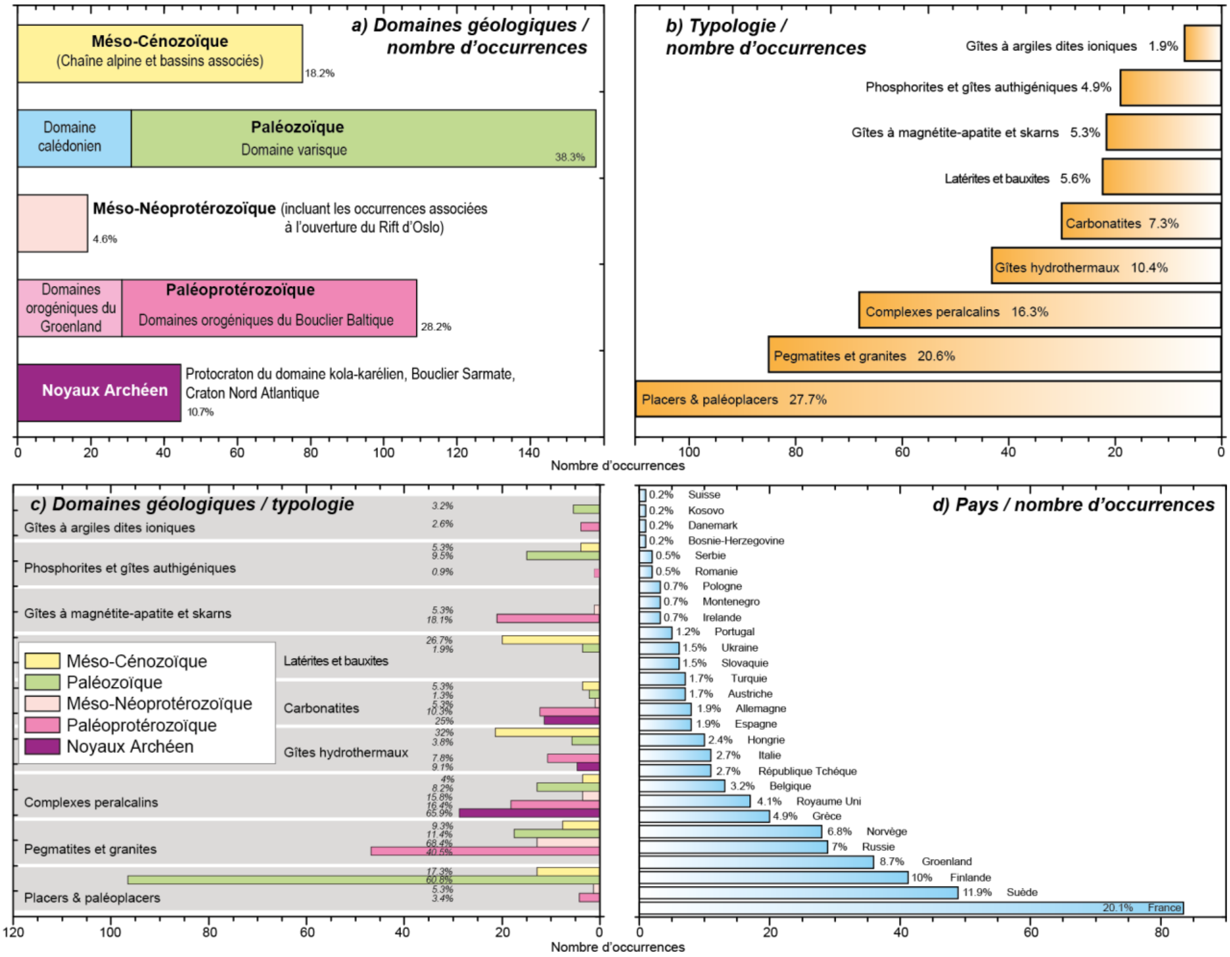

Figure 8 - Distribution des occurrences de terres rares en fonction : a) des grands domaines géologiques ; b) de leur typologie ; c) du types de gîtes (nombre et proportion) en fonction du domaine géologique ; d) du pays.

Concernant les gîtes associés aux carbonatites, la Finlande et la péninsule de Kola en Russie renferment le potentiel le plus intéressant. Les terres rares sont principalement portées par des minéraux tels que l'apatite, la bastnäsite, la monazite et le pyrochlore avec parfois de l'allanite, de la parisite et de l'ancylite. Les principales cibles sont Fen en Norvège (84 Mt @ 1,08 % REO), Storkwitz en Allemagne (4,4 Mt @ 0,45 % REo) et enfin les « monstres » de la péninsule de Kola tels que Afrikanda (627 Mt @ 0,78 %REo) et Kovdor (915 Mt @ 0,48 % REO). Dans certains gîtes, d'importantes accumulations d'apatite peuvent constituer des corps massifs (apatitite) au sein de carbonatites. C'est le cas de la carbonatite de Sokli en Finlande qui avec ses 250 Mt @ 0,5 % REO de minerai d'apatite pourrait également constituer une cible importante pour prospecter les terres rares.

Le stockwerk à fluorite, barytine, bastnäsite et pyrochlore du gîte de Kizilcaören en Turquie (4,7Mt @ 2,78 % REO) correspondrait à un gîte magmatique-hydrothermal en lien avec la mise en place de dykes de carbonatites et de laves silicatées alcalines (phonolites et trachytes).

Le long du rift d'âge Permien d'Oslo, dans la région de Larvik-Langesundfjord, un important champ de pegmatites pourrait constituer un fort potentiel. Les porteurs de terres rares sont abondants : l'allanite, l'ancylite, la bastnäsite, la britholite, la chevkinite, l'eudialyte, la fergusonite, la gadolinite, la loparite, la monazite, la parisite et le xénotime.

La célèbre mine d'Ytterby en Suède appartient au modèle de pegmatites issues de magmatisme de type I. Ce site initialement exploité pour produire la porcelaine suédoise au XVIII^e siècle est en fait le lieu où a débuté l'histoire des terres rares en 1787 avec la découverte d'un minéral inconnu par C.A. Arrhenius et son analyse en 1794 par J. Gadolin qui a trouvé une « nouvelle terre ». En 1797, A.G. Ekeberg a donné le nom « d'yttrium » à ce nouvel élément qui était en fait un mélange de plusieurs terres rares. Ce minéral a par la ensuite été nommé gadolinite.

De façon plus anecdotique, des concentrations notables de minéraux de terres rares ont également été signalées dans les pegmatites des Alpes italiennes.

Concernant les modèles de gisements non conventionnels, il convient de distinguer ceux associés aux skarns, de ceux associés à l'importante province à magnétite-apatite du nord de la Suède. L'histoire des terres rares se poursuit en Suède dans les gîtes de type skarn. Bien qu'initialement exploité pour le fer et le cuivre, le skarn de Bastnäs a également connu une production historique de terres rares où *ca.* 160 t de minerai de bastnäsite ont été produites entre 1860 et 1919.

Les gîtes de type IOA tels que ceux de la province de Kiruna pourraient quant à eux et dans un futur proche valoriser leurs stériles riches en apatite et terres rares (communication LKAB). Enfin l'Europe renferme de très nombreux gîtes hydrothermaux riches en terres rares tels que les fentes alpines, les filons à Zn-Pb-F-Ba du centre du Royaume-Uni. Quelques gisements à fort potentiel notamment en HREO (HREO/LREO > 0,3) sont localisés en Finlande (Katajakangas et Hangaslampi) et en Suède (Olserum).

4.1.2. Les gîtes secondaires

Dans les bassins, les gisements secondaires de type paléoplacers sont généralement d'âge Tertiaire et Quaternaire, même si quelques-uns sont datés du Précambrien (e.g. Péninsule de Nordkinn en Norvège et Trostad en Suède). Le principal minéral rencontré est la monazite, avec parfois du xénotime, de l'allanite, de l'apatite, de l'euxenite, de la fergusonite, de la loparite, du rutile et du zircon (Donnot *et al.,* 1973;. Morteani 1991; Elsner 2007). En Europe occidentale, ces paleo-placers sont principalement caractérisés par la monazite grise enrichie en terres rares intermédiaires (Sm, Eu, Gd), et avec de très faibles concentrations en U et Th (Donnot et al 1973;. Burnotte *et al.,* 1989; Tuduri *et al.,* 2013). Ces monazites sont issues de l'érosion de roches sédimentaires des anciens bassins du Paléozoïque inférieur de l'ouest de l'Europe (France, Pays de Galles, Belgique, République Tchèque, Ibérie). Comme expliqué plus haut, ces gîtes sont de petite taille et sans intérêt économique.
Les phosphorites constituent un autre type de gîtes de terres rares associé aux bassins sédimentaires. Avec des teneurs comprises entre 0,5 et 1 % REO ayant déjà été mises en évidence ailleurs dans le monde (McArthur et Walsh 1984; Jaireth *et al.,* 2014), ce type de gîte présente un réel potentiel en Europe, surtout si l'on considère l'importante ressource en phosphorites du vieux continent bien supérieure à 1 Gt (Notholt *et al.,* 2005). Les grès phosphatés de l'Ordovicien constituent également des cibles intéressantes en Europe tel que le dépôt de Tåsjö en Suède, avec des ressources estimées à 112,5Mt @ 0,18 % REO.

Concernant les gîtes associés au régolithe, le sud-est de l'Europe renferme de nombreuses occurrences de terres rares associées à des processus d'altération et liées à des bauxites et latérites. Ces occurrences offrent un potentiel qui reste à déterminer dans la région des Balkans ainsi qu'en Grèce (Grebnik, Vlasenica, Marmara).

4.2. LES GISEMENTS DE TERRES RARES AU GROENLAND

4.2.1. Les gîtes primaires

La province magmatique hyperalcaline du Gardar, dans le sud du Groenland, est probablement la plus extraordinaire d'entre toutes. Il s'agit d'un ancien rift (1,35 à 1,12 Ga) à l'aplomb duquel s'est mis en place un important cortège de complexes magmatiques (Grønnedal-Ika, Igaliko, Ilímaussaq , Nunarssuit ou Tugtutôg) à fort potentiel car tous minéralisés en terres rares mais également en Nb, Zr ± U. En effet, chaque intrusion recèle un potentiel gisement de classe mondiale tel que le complexe d'Ilímaussaq (Sørensen *et al.,* 2011 ;. Steenfelt 2012) comprenant les gîtes de Kvanefjeld (> 600 Mt @ 1,06 % REO soit près de de 6,5 Mt de REO couplé avec des ressources en uranium), et le gîte de Kringlerne (> 4 Gt @ 0,65 % REO soit près de 28 Mt de REO). Ces complexes alcalins sont principalement constitués de syénite néphélinique, localement associée à des carbonatites.

Toutefois, le plus fort potentiel en terres rares associé aux carbonatites semble localisé dans la partie occidentale du Groenland, dans le craton archéen et la ceinture paléoprotérozoïque de Rinkian. Là de nombreuses occurrences sont décrites, toutes relativement récentes comme Sarfartoq, datée à 565 Ma et contenant ~ 8,3 Mt @ 1,7 % REO ; ou bien Tikiusaaq (158 Ma) et Qaqqarsuk (156 Ma).

Au sud de la ceinture Paléoprotérozoïque de Rinkian, un champ de pegmatites daté à 1,8 Ga, structure toute la zone de Nassuttutata Tasia. Il s'agit d'une zone à fort potentiel bien que les terres rares soient portées par la monazite, l'allanite ou l'apatite.

4.2.2. Les gîtes secondaires

Les occurrences de gîtes secondaires sont extrêmement rares au Groenland à l'exception d'un paléo-placer à monazite (5 Mt @ 1 % REO) d'âge Crétacé et localisé dans la péninsule de Milne Land.

5. Compréhension des processus de minéralisation

5.1. GÉOCHIMIE DES TERRES RARES DANS LES EAUX DE SURFACE FRANÇAISE : UN APERÇU DU CYCLE EXTERNE À TRAVERS L'UTILISATION DES DONNÉES FOREGS

Les données présentées ci-dessous ont fait l'objet d'une publication ;
Armand, R., Cherubini, C., Tuduri, J., Pastore, N. and Pourret, O., Rare earth elements in French stream waters — Revisiting the geochemical continental cycle using FOREGS dataset. Journal of Geochemical Exploration. DOI: 10.1016/j.gexplo.2015.06.006.

Les terres rares sont reconnues pour être des indicateurs du fonctionnement de l'hydrosystème, car elles témoignent des propriétés et des interactions physico-chimiques de leur environnement. Fort de ce constat, cette étude basée sur les données du programme FOREGS a cherché à répondre aux questions suivantes :

i) à l'échelle de la France, la concentration en terres rares des eaux de surface présente-t-elle une organisation spatiale particulière ?

ii) quelles sont les relations entre le contexte géologique, la topographie, le réseau hydrographique et les concentrations en terres rares ?

Ainsi, trois terres rares ont été particulièrement étudiées (*i.e.,* La, Eu et Lu) ainsi que les propriétés physico-chimiques et éléments majeurs de l'eau (*i.e.,* pH, carbone organique, carbonates, Fe, Mn).

Dans un premier temps, un krigeage factoriel multivarié a permis de spatialiser les échantillons. Au-delà de cartographier la variation spatiale des concentrations en terres rares, cette méthode géostatistique permet aussi d'étudier les corrélations observées entre les variables à différentes échelles et de synthétiser la variabilité spatiale à chaque échelle spatiale sélectionnée à travers des facteurs régionalisés. L'analyse de corégionalisation a révélé deux organisations spatiales : **i**) une structure à petite échelle avec une dimension maximale de corrélation de 120 km et **ii**) une structure à grande échelle avec une dimension maximale de corrélation de 250 km.

L'interpolation de ces variables régionalisées par cokrigeage montre ainsi que les terres rares présentent une organisation spatiale identique : les valeurs les plus importantes sont observées dans le bassin aquitain, plus localement dans le couloir rhodanien et certains affluents de la Loire et de la Seine. Le carbone organique et le manganèse montrent une distribution identique. À l'inverse, le pH et les carbonates ont un comportement différent.

Le krigeage factoriel a permis de déterminer les deux facteurs régionalisés qui synthétisent la variabilité conjointe aux deux échelles spatiales sélectionnées. Les deux facteurs à courte échelle expliquent seulement 70 % de la variabilité spatiale alors que les deux facteurs à grande échelle expliquent jusqu'à 97 % de la variabilité spatiale.

Vu sous l'angle des processus de formation des gîtes de terres rares, les résultats de cette étude montrent que les REE sont essentiellement issues de l'altération de roches magmatiques tels que les basaltes et granitoïdes du Massif Central. Au cours de leur transport par les eaux de surface, ces REE vont notamment s'enrichir en Sm, Eu et Gd tout en montrant une nette diminution de l'anomalie négative de Ce qui est corrélée avec la distance à l'exutoire. En effet, plus la distance avec la source augmente, plus les concentrations en REE et en matière organique augmentent suggérant ainsi que la spéciation des REE devient organique. Ainsi, à l'exutoire, le plateau continental de la côte atlantique pourrait être considéré comme un piège potentiel de REE notamment intermédiaires (Sm, Eu, Gd). Dans ce contexte, les sédiments comparables aux boues métallifères sous-marines, représentent une ressource potentielle en terres rares (Kato *et al.,* 2011).

5.2. GENÈSE DES CONCENTRATIONS AUTHIGÈNIQUES À MONAZITES GRISES RICHES EN EUROPIUM DU MASSIF ARMORICAIN

Les données présentées dans cette partie ont fait l'objet de communications. Elles sont, à la date, en cours de valorisation pour soumission à revue de rang A.

Tuduri, J., Chevillard, M., Colin, S., Gloaguen, E., Gouin, J., Potel, S. and Pourret, O., 2013. Formation of monazite-(MREE) from Paleozoic shales: role of host rock chemical composition and organic material. Mineralogical Magazine, 77(5): 2362.

Tuduri, J., Pourret, O., Gloaguen, E., Gouin, J., Potel, S., Dörr, W., Colin, S. and Chevillard, M., 2014. U-Pb age and geochemistry of authigenic monazites of the Armorican Massif. Implications for formation of monazite-(MREE) from paleozoic shales, 24ème Réunion des Sciences de la Terre, Pau, France, pp. 342-343.

Elles ont également fait l'objet de mémoires d'initiation à la recherche réalisés par des étudiants :
Léo Thévenin et Baptiste Vincens 2013 : Caractérisation minéralogique et géochimique des schistes ordoviciens du Grand Fougeray (Massif armoricain) - Mémoire d'Initiation à la Recherche - Institut Polytechnique LaSalle Beauvais.
Artis Kensai et Alexandre Borniche 2013 : Caractérisation minéralogique et géochimique des schistes ordoviciens du Grand Fougeray (Massif armoricain) - Mémoire d'Initiation à la Recherche - Institut Polytechnique LaSalle Beauvais.
Faddy Nassif et Pierre-Marie Bastien 2013 : Caractérisation minéralogique et géochimique des schistes ordoviciens du Grand Fougeray (Massif armoricain) - Mémoire d'Initiation à la Recherche - Institut Polytechnique LaSalle Beauvais.
Virginie Floch et Aymeric Houdus 2014: Caractérisation pétrographique, minéralogique et géochimique des schistes cambro-ordovicicens de la nappe de Pardailhan (Zone sud de la Montagne Noire) - Mémoire d'Initiation à la Recherche - Institut Polytechnique LaSalle Beauvais.
Philippe Boitiau et Kévin Copigny 2014 : Caractéristiques de la minéralogie, de la géochimie et du métamorphisme des schistes cambro-ordoviciens de la nappe de Pardailhan (Montagne Noire, Massif Central) - Mémoire d'Initiation à la Recherche - Institut Polytechnique LaSalle Beauvais.

Le corollaire de l'hypothèse précédemment développée suggère donc que des roches sédimentaires développées dans un contexte similaire à celui exposé plus haut devraient renfermer des concentrations de terres rares présentant des anomalies positives en Sm, Eu et Gd ; ce qui a été montré par de nombreux auteurs. En revanche, l'origine de ces anomalies a été et est toujours âprement discutée afin de savoir si elles résultent de processus endogènes (métasomatisme ou magmatisme) ou de processus diagénétiques (Rosenblum et Mosier, 1983 ; Donnot *et al.,* 1973 ; Lev *et al.,* 1999).

Dans un souci de réévaluation du potentiel de terres rares de la France, les travaux entrepris au cours de cette étude nous ont ainsi conduit à discuter du comportement des terres rares, dans les bassins sédimentaires côtiers, en utilisant les occurrences de monazite grises authigènes, enrichies en europium, et les schistes noirs de l'Ordovicien du Massif armoricain (région du Grand Fougeray, départements de la Loire-Atlantique et de l'Ille-et-Vilaine).

Les résultats de cette étude montrent que les grains de monazite (jusqu'à 2 mm de diamètre) sont principalement caractérisés par leur couleur grise, la présence systématique d'inclusions minérales, l'absence également systématique de cœur hérité, d'un enrichissement notable en terres rares intermédiaires (ou MREE : Sm, Eu, Gd) et de très faibles concentrations en Th et U. Dans le détail, un zonage chimique montre que le cœur des grains est enrichi en MREE (jusqu'à 10 % en poids Sm_2O_3; 1,3 % en poids Eu_2O_3 et 5 % en poids Gd_2O_3), tandis que leurs bordures sont enrichies en LREE. Les modèles de concentration de REE dans ces grains de monazites reflètent également l'abondance de ces mêmes éléments dans les schistes noirs. Ces données couplées avec une étude de cristallinité des argiles associées, suggèrent ainsi que la cristallisation de ces monazites, authigènes, s'est réalisée dans les conditions de la diagenèse profonde aux limites du métamorphisme de très bas grade. Cette hypothèse est renforcée par une datation par méthode TIMS de ces monazites donnant un âge à 384 ± 1,6 Ma, Dévonien moyen tout à fait cohérent avec le modèle présenté.

Il est ainsi suggéré que le plateau continental puisse être considéré comme un piège potentiel pour les ressources en terres rares, définissant un nouveau guide pour l'exploration offshore.

Enfin, les schistes noirs de Bretagne, émergés et soumis à l’érosion depuis des centaines de milliers d’années ont pu libérer la monazite qui a été ensuite concentrée dans des placers @ 2 kg / t.

5.3. ORIGINE DES CONCENTRATIONS EN TERRES RARES DES BOUES OCÉANIQUES DU PACIFIQUE.

Les données présentées dans cette partie ont fait l’objet de communications. Elles sont, à la date, en cours de valorisation pour soumission à revue de rang A.

Melleton, J., Tuduri, J., Pourret, O., Bailly, L. and Gisbert, T., 2014. Rare-earth elements enrichment of Pacific seafloor sediments: the view from volcanic islands of Polynesia, EGU 2014, 27 April – 2 May, Vienna, AU. Geophysical Research Abstracts Vol. 16, EGU2014-15804.

Cette étude repose sur de récents travaux ayant révélé de nouvelles ressources en terres rares dans les boues océaniques des fonds marins du Pacifique et dont l’origine serait liée à l’hydrothermalisme des dorsales médio-océaniques (Kato *et al.,* 2011). Cependant, plusieurs contributions ont également montré que les REE étaient considérablement enrichies dans certains basaltes de la Polynésie française.

Les travaux entrepris dans le cadre du projet ASTER, se sont ainsi concentrés sur des échantillons provenant de l'île volcanique de Tahaa (Sous-le-Vent île, archipel de la Société, Polynésie française). Il s’agit d’échantillons provenant du premier site où des enrichissements majeurs en terres rares dans des roches basaltiques ont été décrits. Les résultats montrent que l’altération météorique de basaltes riches en terres rares a conduit à la néoformation dans des conditions supergènes de de minéraux de terres rares (principalement des phosphates du groupe du rhabdophane $(Ce,La)PO_4{\bullet}(H_2O)$) dans les vésicules du basalte et dans des fractures.

Sur la base de ces observations, nous suggérons que l'enrichissement anormal observé dans les sédiments des fonds marins du Pacifique serait lié à l’érosion et à l’altération des provinces volcaniques anormalement riches en terres rares.

5.4. LE GISEMENT DE TERRES RARES DE MOUNT WELD (AUSTRALIE OCCIDENTALE) : UN EXEMPLE DE GITE ISSU DE L’ALTÉRATION SUPERGÈNE D’UNE CARBONATITE

Les données présentées dans cette partie sont, à la date, en cours de valorisation pour soumission à revue de rang A.
Bailly, L., Tuduri, J., Olivier, M., Shand, B., Carder, M. Lateritization and enrichment processes of the Mount Weld REE-bearing ore body derived from carbonatite (Western Australia). A soumettre @ Economic Geology.

Elles ont également fait l’objet de rapports de recherche réalisés par des étudiants :
Olivier, M., 2015. Caractérisation minéralogique et géochimique de la minéralisation à terres rares contenue dans le profil d'altération latéritique développé à l'aplomb de la carbonatite de Mount Weld, Université d’Orléans, BRGM, Orléans.

Le gisement de Mount Weld en Australie Occidentale est à ce jour, le plus gros gisement de terres rares, hors Chine, développé sur carbonatite (17,5 Mt @ 7,9 % REO). Il contient également des ressources en phosphates, niobium, titane et vanadium. L’essentiel de la minéralisation en terres rares est contenu dans les formations altérées développées à l'aplomb de la carbonatite fraîche sur une puissance variant entre 10 et 70 m. Les études consacrées à ce gisement sont rares et anciennes : Lottermoser, 1987 ; Lottermoser and England, 1988 ; Lottermoser, 1990 ; Middlemost, 1990.

Un échantillonnage des formations accessibles au niveau de la mine à ciel ouvert a été réalisé lors d'une brève visite en Juillet 2014. Plusieurs échantillons ont été prélevés au niveau d'un pointement de carbonatite peu altérée mise à jour lors de l'exploitation dans laquelle la texture magmatique est encore clairement visible. Les autres échantillons proviennent de faciès latéritiques très altérés, de couleur variable, prélevés à différents endroits de l'exploitation. Ces échantillons ont été étudiés en microscopie optique sur lame mince polie, au microscope électronique à balayage, par ICP/MS pour le dosage des éléments majeurs, des traces et des terres rares. Le chimisme des phases minérales présentes a été déterminé à la microsonde électronique et la nature de certaines d'entre elles confirmée par diffraction des rayons X.

Les échantillons de saprolite sont composés principalement de dolomite, d'apatite et de fluorocarbonates de terres rares représentés macroscopiquement par des minéraux millimétriques de couleur rouge. Deux générations de dolomite ont été mises en évidence. La première est représentée par des cristaux automorphes de dolomite dont les clivages sont soulignés par des oxydes de fer qui confère à la roche sa couleur brune. La seconde correspond à des cristaux de dolomite de plus grande taille, limpides, présents sous forme de remplissages géodiques où le quartz est localement présent. Deux générations d'apatite ont également été mises en évidence. Les cristaux les plus précoces sont aciculaires et caractérisés par des teneurs en SrO variant entre 1,35 et 2,80 poids %. La seconde génération, pauvre en strontium, se présente sous forme de cristaux trapus en remplissage des veinules tardives. Des agrégats informes de monazite sont présents dans ces échantillons en remplacement des cristaux d'apatite de première génération. Les fluorocarbonates ont été identifiés comme un assemblage de cristaux de parisite [$Ca(La,Ce)_2(CO_3)_3F_2$] et de bastnäsite [$(La,Ce)CO_3F$].

Les échantillons de latérite montrent des degrés d'altération variables marqués par une augmentation des teneurs en Fe_2O_3 et une diminution des teneurs en CaO et MgO. Les fluorocarbonates de terres rares initiaux, reconnaissables par leur texture, sont toujours présents mais complètement remplacés par des phosphates de terres rares de composition proche du rhabdophane [$(La,Ce)PO_4.H_2O$]. Cette phosphatisation sélective, observée uniquement dans les échantillons de latérite, serait d'origine supergène. Localement, ces phosphates sont eux-mêmes déstabilisés et apparaissent résiduels et ceints d'une auréole d'oxydes de fer et/ou de manganèse riches en Ce.

La somme des terres rares oscillent entre 3 % dans les saprolites à plus de 10 % dans les latérites avec un rapport terres rares légères sur lourdes variant respectivement de 130 à 60. Les spectres de terres rares normalisés aux chondrites mettent en évidence un net enrichissement en terres rares légères qui atteint son maximum pour les échantillons de latérite les plus altérés. Cependant, les spectres obtenus sur les échantillons de saprolite et de latérite restent parallèles suggérant un comportement identique des terres rares légères et lourdes au cours de l'altération.

À ce jour, les principaux porteurs de terres rares identifiés se limitaient à la monazite, au rhabdophane, à la churchite, et à des alumino-phosphates (Lottermoser, 1990). L'assemblage à parisite/bastnäsite et son altération par phosphatisation puis oxydation vient compléter la paragénèse magmato-hydrothermale et supergène de ce gisement et ouvre de nouvelles perspectives d'étude du comportement des terres rares dans la sphère supergène.

6. Conclusion - Évaluation du potentiel en terres rares du continent européen et du Groenland

6.1. SYNTHÈSES ÉCONOMIQUES

Comme expliqué plus haut, l’Europe continentale et le Groenland renferment de nombreuses occurrences de terres rares dont certaines constituent des cibles de premiers plans.

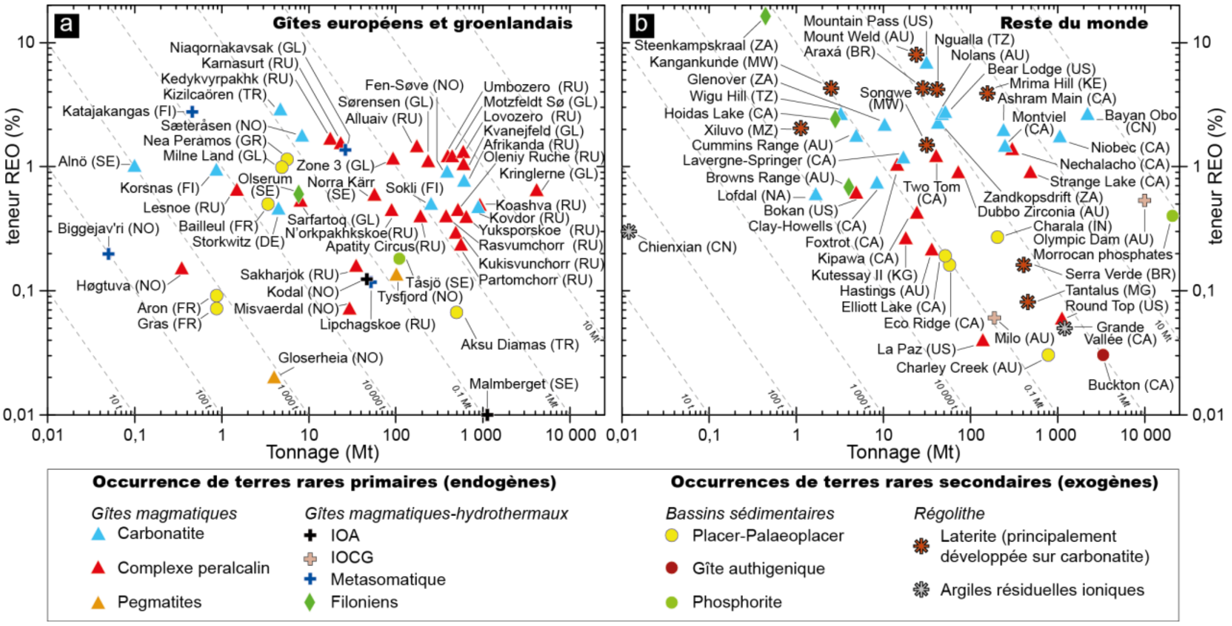

Figure 9 - Relation teneur et tonnage pour les différents types d’occurrences de terres rares localisées en (a) en Europe et au Groenland et (b) dans le reste du monde.

En effet, les figures 9 et 10 permettent la comparaison entre le potentiel économique des gîtes européens et ceux du reste du monde. Si les gisements présentant les plus fortes teneurs en REO ne sont pas localisés en Europe et au Groenland (i.e. Mountain Pass et Mount Weld), cette région offre cependant un potentiel au moins tout aussi intéressant que dans le reste du monde, avec de nombreux gîtes et gisements de classe mondiale.

En conséquent, plusieurs projets d’exploration ont vu le jour en Europe et au Groenland ces dernières années (Figure 10). Parmi les plus avancés, on pourra citer : celui de Norra Kärr (REE, Zr) en Suède détenu par la compagnie Tasman Metals Ltd., celui de Kvanefjeld (U, REE, Zn) au Groenland détenu par la compagnie Greenland Minerals and Energy Ltd., ainsi que celui d’Aksu Diamas (REO, Ti, Zr …) en Turquie détenu par la société AMR mineral and metal. D’importantes campagnes de forage ont accompagné le développement de ces projets, ayant conduit à l’évaluation de ressources et même de réserves pour Norra Kärr, selon le cadre des systèmes JORC et NI43-101. En outre, des études approfondies en métallurgie ont été et sont réalisées afin de valoriser le potentiel en terres rares de nouveaux porteurs minéralogiques comme par exemple l’eudialyte (Norra Kärr) ou la steenstrupine (Kvanefjeld). Compte tenu de leur qualité, ces projets pourraient rentrer en production à l’horizon 2020 et commencer à approvisionner l’Europe en terres rares pour les décennies à venir.

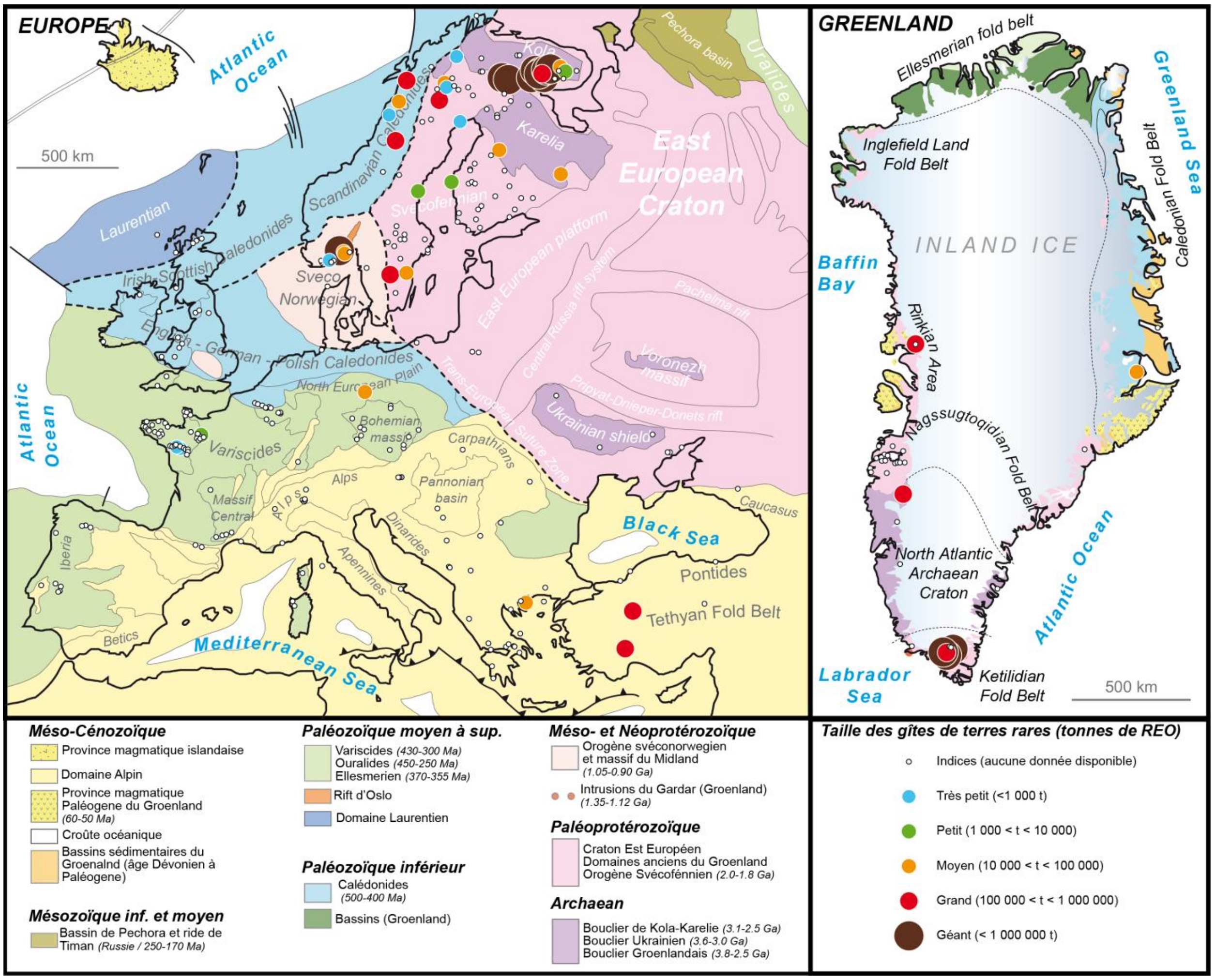

Figure 10 - Taille des occurrences de terres rares en Europe et au Groenland, en tonnes d'oxyde de terres rares, REO.

Il existe également de nombreux autres projets, moins matures car moins bien étudiés en Europe et au Groenland (Figure 11). Même si certains de ces projets peuvent déjà offrir un excellent potentiel (e.g. Olserum en Suède, Fen en Norvège), ils ne constituent pas des cibles prioritaires. Ils continueront à être développés dans les années à venir et constitueront peut-être de futures découvertes sur le plus long terme. Ces projets ne sont donc pas susceptibles d'apporter une contribution significative à l'offre en terres rares avant la fin de cette décennie.

Enfin, l'UE-28 a récemment montré un intérêt croissant pour l'exploration et l'utilisation des ressources des fonds sous-marins compte tenu de la taille considérable de la zone économique exclusive européenne (ZEE) dans le monde (la première). En effet, si les métaux de base sont communs à proximité de sources hydrothermales, les boues des fonds marins océaniques et les nodules de manganèse peuvent également être concentrés en REE. Une étude récente (Kato *et al.,* 2011) a révélé des ressources insoupçonnées dans les sédiments du Pacifique. Ces derniers montrent un taux d'enrichissement en terres rares lourdes bien supérieur aux gîtes de type argiles ioniques, une caractéristique qui augmente considérablement leur intérêt économique. Plus récemment encore, dans le cadre de cette étude, Pourret *et al.,* (2012) et Armand *et al.,* (2015) ont suggéré que le plateau continental Atlantique au large de l'Europe occidentale pouvait constituer un réservoir de terres rares dont le potentiel reste encore à définir.

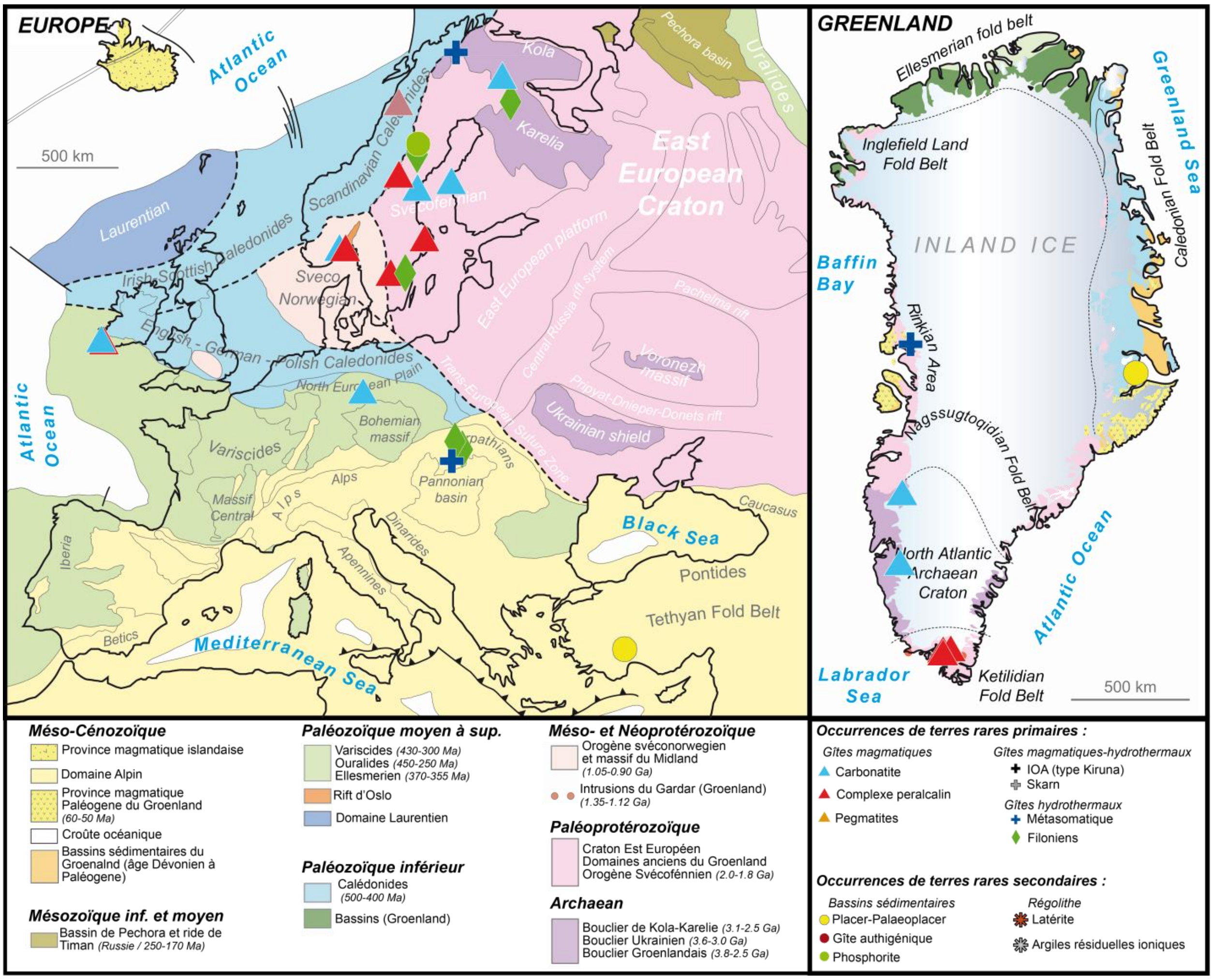

Figure 11 - Localisation des principaux projets d'exploration en Europe et au Groenland.

6.2. SYNTHÈSE GÉOLOGIQUE

L'Europe continentale et le Groenland renferment de nombreuses occurrences de terres rares appartenant à des modèles de gisements variés qu'ils soient conventionnels ou non. D'un point de vue géologique, le potentiel en terres rares est essentiellement localisé dans les domaines de socles anciens à savoir le Bouclier Scandinave et le Groenland (Figure 12). Les modèles de gisements les plus pertinents restent les gîtes de type carbonatites et les complexes (per)alcalins. Cependant, les provinces à pegmatites ayant jusqu'à présent suscitées peu d'intérêt de la part des industriels pourraient renfermer un certain potentiel en terre rares. Le potentiel en terres rares de l'Europe de l'Ouest reste quant à lui très limité et associé à des gîtes de type placers. Si leur taille reste très modeste, ils se caractérisent par leur faible teneur en U et Th.

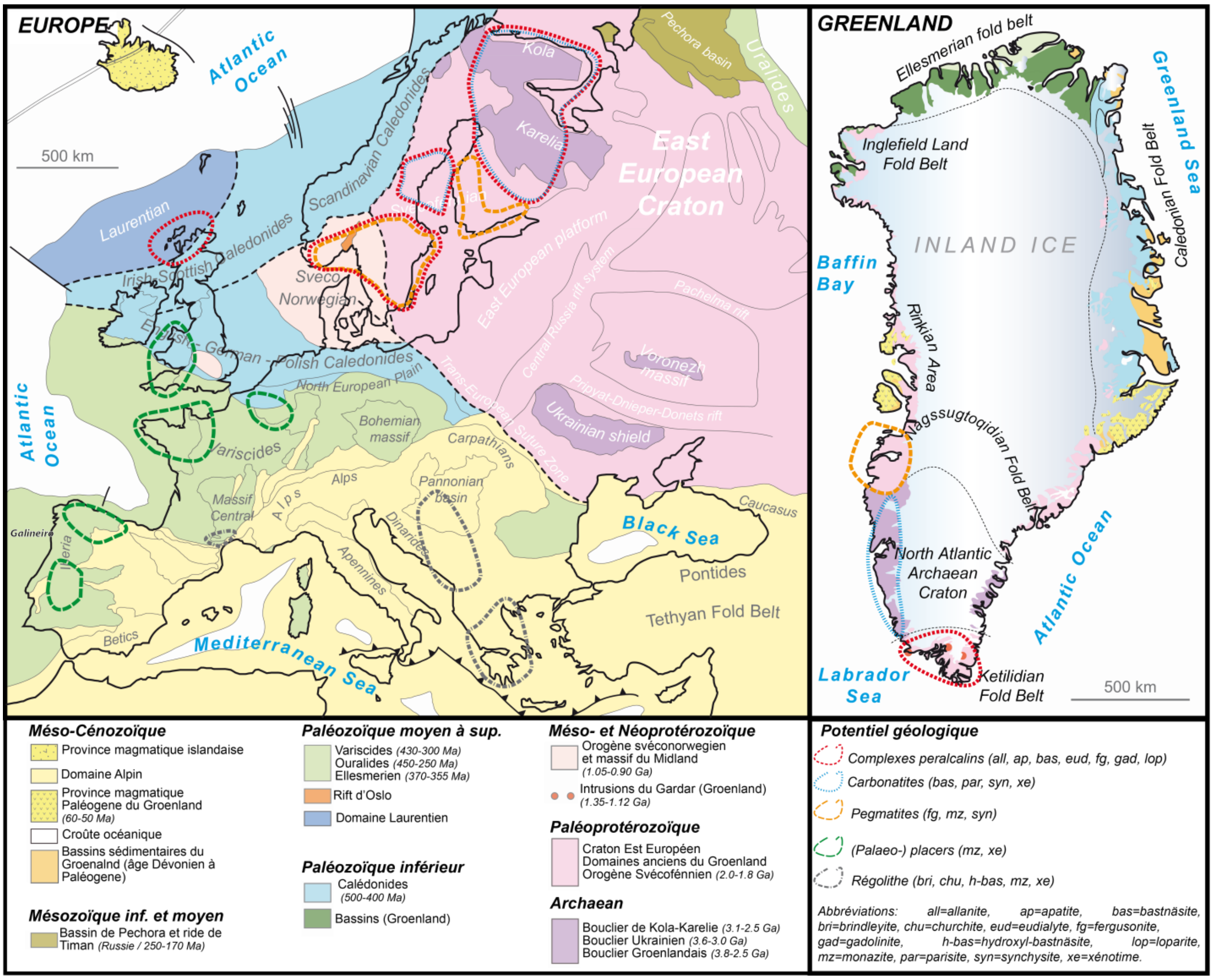

Figure 12 - Potentiel en terres rares de l'Europe et du Groenland.

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Annexe 1

Inventaire des occurrences de terres rares en Europe et au Groenland

Annexe 2

Articles scientifiques : Typologie des gîtes de terres rares de l'Europe et du Groenland et caractérisation du potentiel géologique

Charles, N., Tuduri, J., Guyonnet, D., Melleton, J. and Pourret, O., (2013) - Rare earth elements in Europe and Greenland: a geological potential? An overview. In: E.e.a. Jonsson (Editor), Proceedings of the 12th Biennial SGA Meeting, Uppsala, Sweden, pp. 1698-1701.

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Rare earth elements in Europe and Greenland: a geological potential? An overview

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Abstract. Recently, rare earth elements (REE) have occupied a centre-stage owing to the large volatility of prices and stress occasioned on global markets by limitations of Chinese export quotas. Thus, numerous industries which depend on secured and diversified rare earths sources, now consider REE as critical for new technologies. In response, countries are developing and diversifying their supply sources, with new mining projects located outside China and efforts in the REE recycling domain.

Based on a global geological and metallogenic synthesis, a first review map representing more than 270 REE occurrences and deposits classified by typology in Europe and Greenland is proposed. At first glance, the Baltic Shield and South Greenland constitute the main areas with a strong potential. Indeed, northern Europe is characterised by numerous occurrences linked to alkaline intrusions, carbonatites and pegmatites. In southern Greenland, the Ilímaussaq alkaline complex contains the future world-class Kvanefjeld U-REE-Zn deposit.

While REE are relatively ubiquitous in Europe and Greenland and occur in a variety of geological settings, only the two previously mentioned regions appear to have economic potential. However, progress in the understanding of the REE ore forming processes is required to help better guide exploration and make new discoveries. While recycling technologies should be developed, reliance on extracted sources will continue to be indispensable, especially considering annual growth rates for REE demand, which are around 5%.

Keywords: REE, occurrence, deposit, Europe, Greenland, potential.

1 Rare earths: strategic and critical

Recent years have seen unprecedented volatility concerning prices and the dynamics in the global market of the rare earth elements (REE). Nowadays, numerous industries depend on secured and diversified rare earth sources, which are increasingly considered as critical to a wide range of new technologies (i.e. permanent magnets, energy storage, phosphors *etc.*) and as strategic by numerous states, including among the EU-27. As China is practically a monopoly producer, its recent limitations on export quotas have had a severe economic impact. To overcome this, REE consuming countries are developing and diversifying their supply sources, based on both extracted and recycled sources. With respect to the former, new mining projects in the USA and Australia (e.g. Mountain Pass, Mount Weld) provide welcome alternatives to import from China. Regarding Europe and taking into account Greenland, several new projects are currently being developed in Scandinavia and Greenland (e.g. Norra Kärr, Kvanefjeld). A reliable assessment of current European REE resources and reserves and of future potentials should rely on a better understanding of REE ore-forming processes, taking into account the considerable diversity of deposits and associated geological settings within continental Europe. Relying on a global geological and metallogenic synthesis, notably from the European ProMine Project database, a first review map representing over 270 REE occurrences and deposits, classified by typology in Europe and Greenland, is proposed. Such a synthesis provides a basis for identifying preferential areas for future REE exploration (Figure 1).

2 Typology of rare earths deposits

The term REE is often considered as a misnomer since these elements are quite common in the Earth's crust. The REE can occur in a broad range of geological settings and their concentration and distribution in minerals depend on rock forming, hydrothermal, weathering and other surface processes. REE deposits are broadly divided into two main categories: primary deposits associated with magmatic and hydrothermal processes and secondary deposits concentrated by sedimentary processes and weathering (Kanazawa and Kamitani 2006; Walters et al. 2011; Chakhmouradian and Wall 2012).

2.1 Primary deposits

Primary REE deposits - which represent the bulk of REE production since 1960s - are broadly associated with alkaline-peralkaline igneous rocks and carbonatites. However, REE minerals may be also associated with pegmatites, skarns, Fe oxide-phosphates and quartz-fluorine-bearing veins.

In carbonatites, REE are mainly represented by light-group rare earth elements (LREE, from ^{57}La to ^{64}Gd) occurring in minerals such as bastnäsite, allanite, apatite and monazite (Gupta and Krishnamurthy, 2005). REE deposits associated with alkaline-peralkaline rocks are relatively low-grade (<5 % rare earth oxides REO) although they are commonly enriched in heavy-group rare earth elements (HREE, from ^{65}Tb to ^{71}Lu and also ^{39}Y; Chakhmouradian and Zaitsev 2012). Typical minerals are apatite, bastnäsite, eudialyte, gadolinite and loparite, which are often associated with "exotic" rock names such as ijolite, lujavrite, urtite or melteigite.

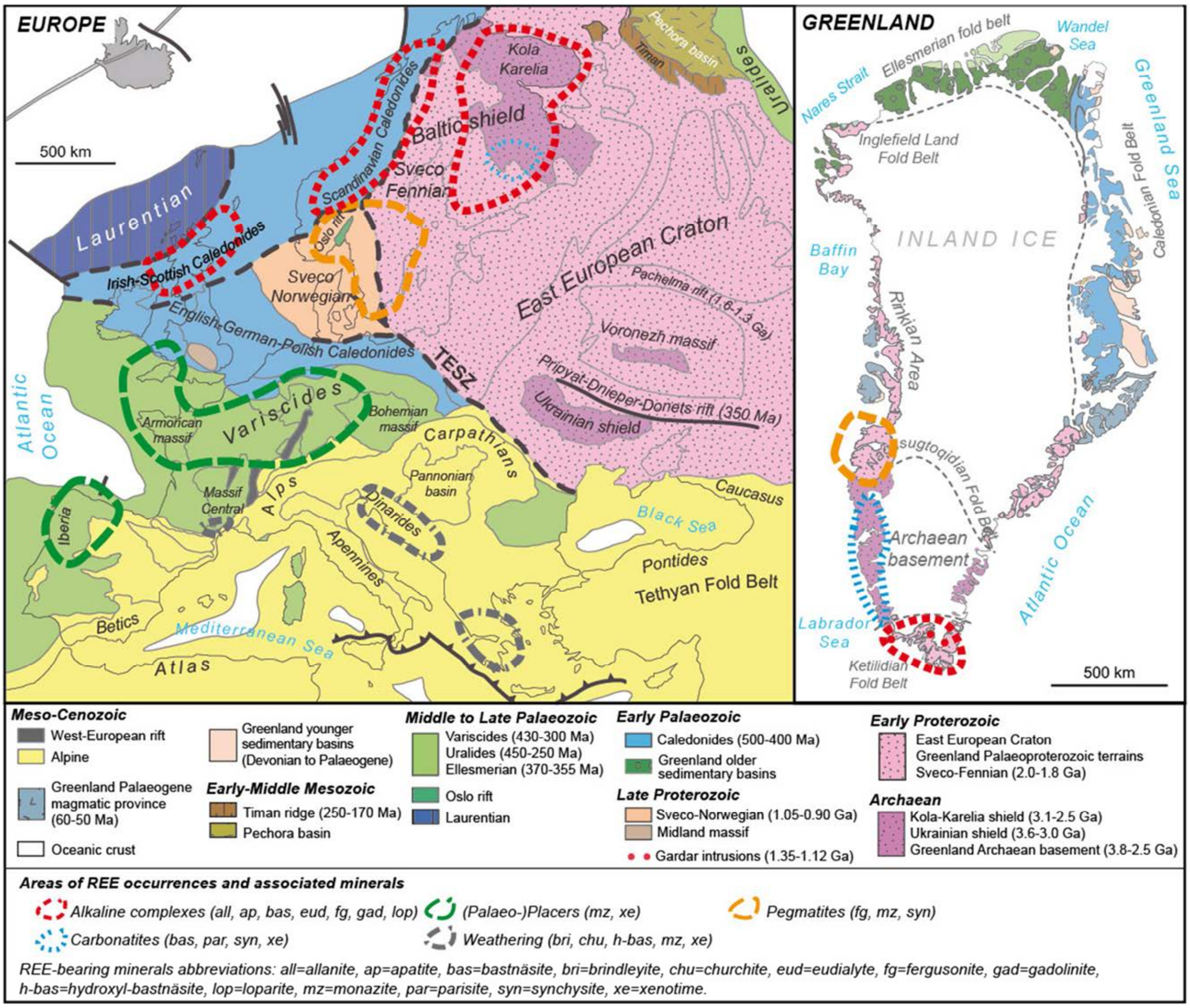

Figure 1. Simplified geotectonic map of Europe and Greenland (modified after Artemieva et al. 2006; Gee and Stephenson 2006; Henriksen 2008) and their potential areas for REE occurrences and deposits. Also indicated are REE-bearing minerals associated with each deposit type.

In addition to alkaline-peralkaline igneous rock deposits, pegmatites containing significant amounts of LREE (allanite, monazite) or HREE (gadolinite) mineralisation can occur.

Moreover, notable REE concentrations are observed within a few iron-oxide-copper-gold (IOCG) deposits or in the magnetite-apatite deposit of the Kiruna district in northern Sweden (Harlov et al. 2002). Such deposits are hosted by a variety of rocks ranging from intrusive igneous to volcanic and sedimentary rocks, with REE-bearing minerals such as apatite or allanite.

It is worth to mention some other REE deposits associated with sedimentary rocks, e.g. fluorite-baryte mineralisations (disseminated in veins and breccia, with synchysite and parisite) or U-deposits.

2.2 Secondary deposits

Secondary deposits represented the bulk of REE production prior to the 1950s (100 kt), especially from monazite-bearing placers (Orris and Grauch 2002). Secondary deposits are mainly the result of sedimentary remobilization and weathering processes: placers, REE-bearing clays and laterites including ion-adsorption type REE deposits. The latter are currently only mined in southern China for HREE.

Placer deposits are accumulations of heavy minerals in sands and gravels by gravity separation during sedimentary processes. Placers are generally Tertiary and Quaternary in age, although a few are dated as Precambrian. Main REE-bearing minerals are monazite (with or without xenotime), fergusonite, euxenite, allanite and loparite (Donnot et al. 1973; Morteani 1991; Mohanty et al. 2003; Elsner 2007).

Weathering processes lead to the breakdown of many rock-forming minerals, the leaching of certain elements (Mg, Ca) and the residual enrichment of less mobile elements (Fe, Al). Thus weathering of initially REE-enriched rocks (e.g. carbonatite) can provide residual weathering REE deposits (e.g. laterites, bauxite; Lottermoser 1990) with new supergene minerals (e.g. phosphates such as monazite) and high-grades (10-25% REO).

Another type of residual REE deposit has been described: REE-bearing clays, termed ion-adsorption clays (Chi and Tian 2008). These low-grade deposits

(0.03-0.35% REO) are HREE-rich and often associated with weathered REE-enriched granites, where REE are adsorbed by clay minerals such as kaolin or halloysite.

3 Geological potential: an overview

3.1 Rare Earths in Europe

In Europe, primary deposits or occurrences are mainly represented by alkaline complexes and carbonatites, located in northern Europe. Indeed, at first glance, the Baltic shield and Kola Peninsula constitute the main areas with strong geologic potentials. Alkaline intrusions such as Norra Kärr (Sweden) can constitute new projects for REE mining in Europe. This intrusion, represented by a nepheline syenite, contains an inferred REE mineral resource of 60.5 Mt @ 0.54% REO (Tasman Metals, 2013). Other potential deposits linked to alkaline intrusions are Tasjö (Sweden), Katajakangas and Otänmaki (Finland), Kodal and Saeterasen (Norway). Moreover, the Kola Peninsula exhibits the both well-known Khibina and Lovozero alkaline complexes (Sørensen 1997; Arzamastsev et al. 2006) with reserves estimated at 1,000 Mt @ 0.8-1.5% REO (Kogarko 1995 *in* Orris and Grauch 2002). In the north-west of Scotland, several occurrences associated with British Caledonian alkaline intrusions are mentioned close to Loch Borralan, Loch Ailsh and Ben Loyal (Shaw and Gunn 1993; Young et al. 1994). To the latter can be added occurrences related to British Tertiary igneous rocks, such as Skye and St-Kilda. With respect to carbonatites, examples are the Fen Nb-Ta deposit (Norway), with several REE-bearing minerals (monazite, bastnäsite, synchysite), and also the Sokli carbonatite in Finland. Close to the Permian Oslo rift, the Larvik-Langesundfjord region exhibits numerous pegmatites with REE-bearing minerals. Note that anecdotic concentrations of REE-bearing minerals have been reported in pegmatites in the Italian Alps. In northern Sweden, the Kiruna apatite-iron ore deposit has REE resources roughly estimated to ~5.6 Mt @ 0.5% REO (Parák 1973). It is also worth noting the occurrence of REE observed within Zn-Pb-F-Ba deposits in the North Pennine ore field (England; Bau et al. 2003).

Secondary deposits or occurrences in Europe are mainly represented by grey monazite palaeoplacers, associated with Ordovician sediments of Palaeozoic basins (i.e. western France, Wales, Belgium, Czech Republic) and linked to the Variscan orogeny. Current to recent placers that might constitute interesting targets are found in Denmark (Hanstholm), Germany (Cuxhaven) or Poland (Slupsk), and would deserve to be better explored and qualified. Potential occurrences related to weathering processes should not be overlooked, e.g. REEs related to bauxite deposits in the Balkans and Greece (Grebnik, Vlasenica, Marmara; i.e. hydroxyl-bastnäsite, brindleyite, goyazite), or in the south of France. Investigations could be carried out on clays from Permian-Triassic terrains, phosphorous levels within certain Palaeozoic sediments (e.g. southern France) and on F-Ba deposits of the French Massif Central.

3.2 Rare Earths in Greenland

In view of current proposed projects, it has been suggested that Greenland may represent a REE potential capable of meeting 25% of global demand.

Primary deposits or occurrences mainly consist of the Gardar alkaline complexes. Located in South Greenland, the Gardar Province (1.35-1.12 Ga) contains alkaline complexes that exhibit main occurrences with potentially future world-class REE deposits, such as Kvanefjeld in the Ilímaussaq intrusion (6.6 Mt total REO (TREO) coupled with U resources), and the Kringlerne (20 Mt TREO) or Motzfeldt intrusions (Sørensen et al. 2011; Steenfelt 2012). The Gardar Province contains other alkaline intrusions that can be interesting for REE potential, such as Grønnedal-Ika, Igaliko, Nunarssuit or Tugtutôg. Those alkaline complexes mainly consist of nepheline syenite, locally associated with carbonatite, and are intruded into the Julianehab batholith in relation with the Ketilidian fold belt. Alkaline intrusions also occur to the eastern part of Greenland: the Gardiner complex (50 Ma) and Kap Simpson. In the western part of Greenland, in the Archaean craton and Rinkian Palaeoproterozoic mobile belt, many promising occurrences of carbonatites and pegmatites are described. For example the Sarfartoq carbonatite, dated at 565 Ma, contains ~14 Mt @ 1.51% REO (Secher and Larsen 1980). Besides, the Jurassic Qaqqarsuk (156 Ma) and Tikiusaaq (158 Ma) carbonatites show REO contents of 2.4 and 9.6%, respectively. South of the Rinkian Palaeoproterozoic mobile belt, pegmatites dated at 1.8 Ga, largely occur in the Nassuttutata Tasia area. Main REE-bearing minerals are monazite, allanite and apatite.

There are currently few descriptions of secondary deposits or occurrences in Greenland. One occurrence is Milne Land, located in eastern Greenland, which is a Cretaceous monazite-bearing palaeoplacer.

4 Economic considerations

Parallel to current efforts to find alternative extracted sources of REEs, a significant effort is devoted developing technologies for recycling REEs in products. Binnemans et al. (2013) provide a review of current technologies for the three market sectors that appear to provide the most potential in terms of recycling: permanent magnets, NiMH batteries and phosphors. A global perspective of REE flows and stocks in the world economy is provided by Du and Graedel (2011a), using material flow analysis. The diagrams for several REEs illustrate the orders of magnitude of flows between various compartments of the economy (manufacture, use, etc.) but also stocks accumulated in the use compartment (Du and Graedel 2011b). These data suggest accumulated (and hence potentially recyclable) stocks in the economy on the order of 440,000 t REE in 2007. According to Lynas (2010), world rare earth demand in 2010 was on the order of 136,100 t (i.e. approx. 115,000 t REE). Even assuming significant progress in REE recycling technologies, given the annual rate of growth of REE demand (on the order of 5%; Alonso et al. 2012), recycling of accumulated stocks in the economy cannot be expected to satisfy demand. In a growth based economy, there is a gap between demand and the "offer" provided by the waste stream, due to the lifetime of products in the economy (see e.g. Grosse 2010). Therefore, REEs will need to be extracted in the future, in order to satisfy in particular the demand for clean technologies. Recycling, however, especially of certain HREEs (Dy, Tb, etc.) but also Nd, is essential to reduce the so-called "balance problem" (Binnemans et al. 2013), which generates an excess of the more abundant elements (La, Ce) as a result of mineral extraction. The potential from recycling can be compared to that of mining projects cited previously. For three European projects alone (Kringlerne, Kvanefjeld and Norra Kärr) the potential (resources + reserves) is on the order of 30 Mt REO.

5 Perspectives for exploration?

The review of rare earth occurrences in Europe and Greenland illustrates the relative ubiquity of REEs in various geological settings. Currently, however, the most promising potential is only concentrated in southern Greenland and in the Baltic shield, with a few very large deposits. Further work on REE ore-forming processes applied to specific European geological settings could help guide exploration and allow new discoveries (e.g. Permian-Triassic clays in western Europe, F-Ba deposits in the French Massif Central, phosphorous levels of Palaeozoic sedimentary series, alkaline intrusions of the Gardar complex in Greenland, etc.).

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Europe’s rare earth element resource potential: an overview of metallogenetic provinces and their geodynamic setting

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Abstract

Security of supply of a number of raw materials is of concern for the European Union; foremost among these are the rare earth elements (REE), which are used in a range of modern technologies. A number of research projects, including the EURARE and ASTER projects, have been funded in Europe to investigate the REE supply chain. Although the REE are not currently mined in Europe, potential resources are known to be widespread, and many are being explored. The most important European resources are associated with alkaline igneous rocks and carbonatites, although REE deposits are also known from a range of other settings. Within Europe, a number of REE metallogenetic belts can be identified on the basis of age, tectonic setting, lithological association and known REE enrichments. This paper reviews those metallogenetic belts and sets them in their geodynamic context. The most well-known of the REE belts are of Precambrian to Palaeozoic age and occur in Greenland and the Fennoscandian Shield. Of particular importance for their REE potential are the Gardar Province of SW Greenland, the Svecofennian Belt and subsequent Mesoproterozoic rifts in Sweden, and the carbonatites of the Central Iapetus Magmatic Province. However, several zones with significant potential for REE deposits are also identified in central, southern and eastern Europe, including examples in the Bohemian Massif, the Iberian Massif, and the Carpathians.

Keywords

Rare Earth Elements, Europe, EURARE, alkaline igneous rocks, carbonatite, metallogenetic belts

1. Introduction

The rare earth elements (REE) are a group of 17 chemically similar elements (the lanthanides, scandium (Sc) and yttrium (Y)). Here we focus on the lanthanides and Y, which behave in similar ways in most environments in the Earth's crust. They are typically divided into light (LREE) and heavy (HREE) rare earth elements. LREE and HREE are variably defined: we follow the EU definition of the LREE (EC, 2014) as lanthanum to samarium, and the HREE as europium to lutetium plus yttrium. Some members of this group are vital components in much modern technology, from high-strength magnets used in wind turbines, hard disk drives and engines in electric cars, to phosphor-based fluorescent lighting, smartphone screens and batteries. Demand for these elements is thought to be growing at a rate of approximately 5-10% per year (Hatch, 2012, Massari and Ruberti, 2013) although rapid technological development means that accurate prediction is difficult. Recycling of scrap consumer electronics and technical industrial components will increasingly contribute to REE supply in the future (Binnemans et al., 2013), but is unlikely to be able to meet increasing demand (Du and Graedel, 2011), and thus mining of natural deposits is expected to continue as the major source for REE. At the time of writing, almost 90% of all REE entering the global market are produced in China (Wübbeke, 2013), and the EU has to import virtually all its REE, either as raw materials or as products such as batteries and magnets (Wall, 2014, Guyonnet et al., 2015). For this reason, the European Commission has recently identified the REE, particularly the HREE, as critical materials with a significant risk to supply (EC, 2014). Detailed recent research highlights neodymium (Nd), europium (Eu), dysprosium (Dy), terbium (Tb) and yttrium (Y) as the most critical of all of the REE, because of their use in the important magnet and phosphor markets (Du and Graedel, 2013), although the criticality of Eu, Tb and Y is likely to change as LEDs increasingly replace phosphors (Guyonnet et al., 2015).

This paper is a product of the EURARE project, which is funded by the European Commission under the Seventh Framework programme to set the basis for development of a European REE industry; and the ASTER project granted by the French national research agency (ANR) to understand REE flows and stocks in Europe. The EURARE project aims to assess the potential for REE resources in Europe, and to develop new, efficient and sustainable methods for processing of potential European REE ores. Such raw material processing is complex, comprising a beneficiation step to concentrate REE minerals from the ore, extraction of the rare earth oxides from their host minerals to produce a mixed rare earth concentrate, and subsequent metallurgical separation into individual rare earth metals. Once a rare earth deposit is identified, its geology and mineralogy must be fully characterised as beneficiation methods have to be tailor-made for each deposit, and are dependent on properties such as mineralogy, textures and grain size of the ore (Jordens et al., 2013). The first step for the EURARE and ASTER projects has thus been a review of all potential European REE resources and an assessment of which REE deposits deserve further research and characterisation. This review paper presents an overview of the main natural REE occurrences and prospects in Europe, and identifies the areas with most potential for future exploration and development.

Although the majority of the rare earth elements were originally discovered in European samples, chiefly from the Bastnäs and Ytterby mines in Sweden (Gadolin, 1794, Hisinger and Berzelius, 1804, Williams-Jones et al., 2012) there is no recent history of REE mining in Europe. Exploration over the last decade has identified some major REE deposits, particularly in Greenland and the Fennoscandian shield, but it is likely that more extensive primary resources of the REE remain to be identified. The partners in the EURARE and ASTER projects (including the geological surveys of Denmark and Greenland, Sweden, Norway, Finland, France, Greece and the United Kingdom) have critically reviewed both published and unpublished data to develop the overview provided here. Individual REE occurrences were identified based on the criterion that the REE are notably enriched above normal crustal abundances, but some occurrences are only small in size and therefore unlikely to be economic. ‘Europe’ in this context is considered to include EU countries and candidate countries, plus Norway, Switzerland, and Greenland. Russia and Ukraine are not included in this work.

2. Overview of the geological setting of REE mineralisation in Europe

Despite their name, the rare earth elements are not all particularly rare in the earth’s crust; the name reflects the difficulty of separating them into the native metals, and the fact that some members of the group are indeed rare (Chakhmouradian and Wall, 2012). They occur in small amounts in all parts of the Earth's crust in a wide range of tectonic settings, and are widely used for petrogenetic studies. Development of a potentially economic rare earth element resource requires that they are concentrated significantly above background levels. Enrichment of the REE may occur through primary processes such as magmatic processes and hydrothermal fluid mobilisation and precipitation, or through secondary processes that move REE minerals from where they originally formed, such as sedimentary concentration and weathering. Natural rare earth element deposits and occurrences may thus be divided into primary (high-temperature) and secondary (low-temperature) deposit types.

The most important primary deposits with high grade and tonnage are typically associated with alkaline-peralkaline igneous rocks and carbonatites formed in extensional intracontinental rifts (Chakhmouradian and Zaitsev, 2012, Wall, 2014). Primary REE concentrations can also be formed in a range of other geological settings, often associated with granites and pegmatites or with hydrothermal systems, and more rarely in metamorphic or diagenetic settings. Erosion or weathering of any of these primary enrichment types may produce secondary deposits such as placers and ion adsorption deposits (Wall, 2014). In a global context, the bulk of the world's REE are currently derived from carbonatites, notably Bayan Obo in China; these deposits are typically high-grade, but LREE-dominated (Chakhmouradian and Wall, 2012, Wall, 2014). REE deposits associated with alkaline igneous rocks are typically lower grade but with larger tonnage and a higher content of the most critical HREE (Wall, 2014).

Formation of REE deposits in alkaline to peralkaline igneous rocks and carbonatites is typically due to magmatic and/or hydrothermal processes (Wall and Mariano, 1996, Kogarko et al., 2002, Salvi and Williams-Jones, 2006, Schilling et al., 2011, Sheard et al., 2012, McCreath et al., 2012). Alkaline silicate and carbonatite magmatism is associated with small degrees of partial melting of enriched mantle, potentially derived either from metasomatised lithospheric mantle or from mantle plumes (Figure 1), or from interaction between the two (Downes et al., 2005, Wilson and Downes, 2006, Ernst and Bell, 2010). Further evolution of these small-degree partial melts in a near-closed system is typically needed to produce highly evolved igneous rocks enriched in REE minerals. Notably, many important REE deposits are associated with extremely peralkaline igneous rocks containing complex Na-K-Ca-(Fe, Zr, Ti) silicates such as eudialyte-group minerals and aenigmatite that are commonly also enriched in the REE; such rocks are termed 'agpaitic' (Sørensen, 1997, Marks et al., 2011). In contrast, in most other felsic igneous rocks the REE are hosted in accessory minerals such as zircon, allanite, apatite and monazite, and these rocks are termed 'miaskitic'. Key REE minerals within carbonatites include bastnäsite, parisite, synchysite, monazite, pyrochlore and many others (Wall and Mariano, 1996). Major REE-bearing minerals found in European deposits are listed in Table 1.

The main REE metallogenetic provinces in Europe (Figure 2) are those areas where extensional tectonics and introduction of enriched mantle melts have produced alkaline silicate and carbonatite magmatism. Major REE deposits are currently known where the plutonic complexes at depth in continental rift zones have been exposed by erosion (Goodenough et al., 2014). The most notable of these are the Mesoproterozoic Gardar Province of south-west Greenland (Upton et al., 2003) and the Protogine Zone, a major, multiply reactivated, in part extensional structure in southern Sweden (Åberg, 1988, Andréasson and Rodhe, 1990). Both of these zones currently host advanced REE exploration projects. Several intracontinental rift-related provinces of Palaeozoic age occur in Europe, including the Devonian Kola Alkaline Province, which extends from Russia into Finland, and the Permo-Carboniferous Oslo Rift in Norway. The Kola Alkaline Province contains some large peralkaline igneous complexes (Downes et al., 2005) that represent major Russian REE resources, but these lie outside the geographical scope of this paper.

Some episodes of European rifting have progressed to continental break-up and development of a new ocean, notably the formation of the Iapetus Ocean during the Neoproterozoic (Svenningsen, 2001), and the opening of the North Atlantic from the Jurassic into the Cenozoic (Saunders et al., 2013). Such rift phases are typically associated with large volumes of magmatism, but central complexes with alkaline compositions are rare, although isolated carbonatite bodies and dyke swarms are known.

Localised rifting and alkaline magmatism have developed periodically across much of central and southern Europe from the Triassic into the Cenozoic, both to the north of the Alpine collision zone and around the margins of the Mediterranean (Wilson and Downes, 2006). In these areas, alkaline volcanic rocks are typically exposed at the surface; the central complexes that might contain significant primary REE resources are still likely to be hundreds of metres to kilometres below the surface. In general, the major known potential for REE resources around the Mediterranean is dominated by secondary deposits such as bauxites.

Potential REE deposits can also be associated with magmatic and hydrothermal activity in other tectonic settings away from intracontinental rift zones. The most notable of these occur in the Palaeoproterozoic Bergslagen province in Sweden, including the Bastnäs deposits where the LREE were first discovered. These deposits are considered to have formed through reaction of carbonates with fluids derived from subduction-related magmas (Holtstam et al., 2014, Jonsson et al., 2014). There are a number of other areas in Europe where alkaline magmatism has developed towards the end of an orogenic cycle, such as in the Caledonides, and these areas may also contain localised REE enrichments (Walters et al., 2013).

No significant secondary REE deposits with high tonnage and high grade are currently known in Europe, but at a number of localities erosion and weathering processes have formed low-grade REE concentrations that have economic potential because of their relative ease of processing. These include heavy mineral placers, particularly along the Mediterranean coastlines, and bauxites in many parts of southern Europe. In China, and other parts of the world that have experienced tropical weathering, the REE are known to be enriched in weathered ion adsorption clay deposits (Kynicky et al., 2012). However, studies of weathered granitic rocks in Europe have shown no evidence of REE upgrading during the weathering process (Höhn et al., 2014).

3. REE metallogenetic belts in Europe

The EURARE project has identified approximately 100 distinct REE occurrences and deposits across Europe. Some of these are recognised mineral deposits that have been actively explored, and in some cases have estimates of the contained REE resources. Other localities, described here as occurrences, are noteworthy due to either high REE contents or the presence of abundant REE minerals. These occurrences may be potential REE deposits, but further research and exploration are needed. Here we group these deposits and occurrences into key metallogenetic provinces for the REE within Europe on the basis of age, tectonic setting and genetic type (Figure 2), and summarise their geodynamic context.

3.1 Archaean to early Palaeoproterozoic alkaline rocks and carbonatites

No significant REE deposits of Archaean to early Palaeoproterozoic age are known in Europe, and indeed there are few alkaline igneous rocks of this age. Rare examples of alkaline magmatism include the c. 3000 Ma Tupertalik carbonatite in west Greenland (Figure 3) (Bizzarro et al., 2002); the c. 2700 Ma Skjoldungen Alkaline Igneous Province of SE Greenland, which includes nepheline syenites and carbonatites (Nutman and Rosing, 1994, Blichert-Toft et al., 1995); the c. 2600 Ma Siilinjärvi carbonatite in Finland (Figure 4) (Tichomirowa et al., 2006, Rukhlov and Bell, 2010); and the c. 2050 Ma Katajakangas alkaline gneiss in Finland (Sarapää et al., 2013). Apatite is currently mined at Siilinjärvi as a phosphate resource. The main rock types at Siilinjärvi are enriched in REE (Hornig-Kjarsgaard, 1998), and REE-hosting minerals in the carbonatite and associated "glimmerite" include monazite-(Ce), pyrochlore-group minerals, LREE-bearing strontianite and REE-bearing Ti-Nb-phases (Al-Ani, 2013). The Katajakangas gneisses contain mineralised layers rich in zircon, bastnäsite, columbite and thorite, and an informal resource estimate suggests 0.46 million tonnes (Mt) grading 2.4% total rare earth oxides (TREO) (Sarapää et al., 2013).

3.2 Palaeoproterozoic: the Svecofennian Belt

Magmatic and hydrothermal REE deposits are associated with many parts of the Svecofennian orogenic belt, which represents the earliest of Europe's distinct REE metallogenetic provinces. This belt formed during accretion and continental collision leading to amalgamation of the supercontinent Columbia (Nuna) in the Palaeoproterozoic (2000-1700 Ma) (Korja et al., 2006, Roberts, 2013). During this period, subduction around the margins of the growing supercontinent drove extensive igneous activity and also the generation of significant base and precious metal deposits. The tectonomagmatic belts generated in Europe at this time include the Svecofennian and Kola-Karelian of Fennoscandia, the Laxfordian in the Lewisian Gneiss Complex of the UK, and the Ketilidian and Nagssugtoqidian belts in Greenland (Zhao et al., 2002, Lahtinen et al., 2008), but important REE deposits and occurrences are only known from the Svecofennian. In this belt, calc-alkaline magmatism was followed by widespread late-orogenic alkaline magmatism in the waning stages of the Svecofennian orogen (also termed the Svecokarelian orogen). The magmatism was associated with the development of significant hydrothermal activity.

Historically, the most important REE occurrences in Sweden were the Bastnäs-type deposits (Geijer, 1961) and the Ytterby pegmatite in the Bergslagen region (Figure 4), which provided the samples from which many of the REE were originally isolated (Williams-Jones et al., 2012). The Bastnäs-type deposits occur along a narrow zone that stretches for about 100 km NE-SW (the 'REE-line', Figure 5; Jonsson et al. (2014)), and were likely the first deposits in the world to be mined explicitly for REE extraction. They are situated within hydrothermally altered Palaeoproterozoic (1910-1880 Ma) felsic metavolcanics and metasedimentary rocks that formed in a continental back-arc setting (Allen et al., 1996, Holtstam et al., 2014). These REE deposits can be subdivided into two types: one LREE-enriched, in the Riddarhyttan-Bastnäs area, and the other also showing enrichment in the HREE + Y, in the Norberg district (Holtstam and Andersson, 2007). Both types are iron-rich, skarn-type REE deposits associated with metasomatised marble horizons, and formed during hydrothermal activity associated with felsic magmatism (Holtstam et al., 2014). Historical mining in the area has typically focused on iron ore, with minor production of REE. The LREE subtype was mined at Bastnäs, where the key ore minerals included cerite-(Ce), ferriallanite-(Ce), törnebohmite-(Ce) and bastnäsite-(Ce), occurring in an amphibole-rich skarn associated with magnetite, haematite, and sulphides (Holtstam et al., 2014, Jonsson et al., 2014). The HREE-enriched subtype in the Norberg district is more highly enriched in Mg and F, and the REE minerals include fluorbritholite-(Ce), västmanlandite-(Ce), dollaseite-(Ce), gadolinite-(Ce) and gadolinite-(Y) (Holtstam et al., 2014, Jonsson et al., 2014).

Iron oxide-apatite deposits of Kiruna type in the Svecofennian belt are also enriched in the REE (Frietsch and Perdahl, 1995, Smith et al., 2009, Jonsson et al., 2013). These include Kiirunavaara (Kiruna) and Malmberget in the Norrbotten region of northern Sweden, and the Grängesberg-Blötberget deposits in Bergslagen, south central Sweden. The origin of these deposits, whether orthomagmatic or hydrothermal, continues to be debated. Recent work suggests that the Kiruna ores formed during the period 1920-1860 Ma, through hydrothermal alteration of volcanic rocks by high salinity fluids, with subsequent reworking of the mineralisation until around 1750 Ma (Smith et al., 2009). An orthomagmatic origin has also been suggested for these deposits (Jonsson et al., 2013), and in the case of the Grängesberg deposit, ore formation is considered to have taken place prior to 1895 Ma (Högdahl et al., 2013). The deposits are associated with either sodic alteration (albitisation) or potassic alteration. Although largely known as iron ore deposits, the magnetite-dominated ores host high concentrations of REE in fluorapatite, monazite-(Ce), allanite-(Ce), xenotime-(Y) and minor REE fluorcarbonates (Harlov et al., 2002, Jonsson et al., 2013, Majka et al., 2013). Albitised, REE-enriched felsic volcanic rocks of Palaeoproterozoic age at Biggejavri in northern Norway are likely to have been affected by hydrothermal alteration leading to albitisation at a similar time.

At the southern end of the Svecofennian orogen, Paleoproterozoic metasedimentary rocks of the Västervik formation contain heavy-mineral layers, which may represent original placer deposits that have been variably affected by regional metamorphism, metasomatism and REE remobilisation (Reed, 2013). Potentially related to these palaeoplacer deposits are the REE-enriched biotite-magnetite-apatite veins of the Olserum area, which occur within Västervik formation metasedimentary rocks cut by granitoids belonging to the Transscandinavian Igneous Belt (Högdahl et al., 2004). In these veins, REE are mainly hosted in fluorapatite, monazite-(Ce), xenotime-(Y) and ferriallanite-allanite (Ce). The Olserum deposit has an NI-43-101 compliant indicated resource of 4.5 Mt at 0.6% TREO, and an inferred resource of 3.3 Mt at 0.63% TREO (using a TREO cut-off of 0.4%) (Reed, 2013).

The end-Svecofennian alkaline magmatism, around 1800 Ma, included both alkaline silicate intrusions and carbonatites. In Finland, the Korsnäs swarm of carbonatite dykes is dated at c. 1830 Ma, and cuts c. 1900 Ma gneisses (Sarapää et al., 2013). The largest of these dykes was mined for Pb and REE in the 1960s, with the REE chiefly hosted in apatite, monazite, allanite, ancylite, britholite and bastnäsite (Al-Ani et al., 2010, Sarapää et al., 2013). Other carbonatite dykes of similar age are known in Finland, including the Halpanen calcite carbonatite dyke emplaced at c. 1792 Ma (Rukhlov and Bell, 2010), the Naantali carbonatite at c. 1796 Ma (Woodard and Hetherington, 2014), and the Petäiskoski/Juuka carbonatite dykes. All these carbonatites are LREE-enriched, have similar mineralogy, and are typically associated with marginal zones of sodic-potassic alteration (fenitisation) (Woodard and Hetherington, 2014).

Late-orogenic alkaline to calc-alkaline intrusions also formed within the Svecofennian belt, including numerous small shoshonitic (highly potassic) intrusions in southern Finland that show LREE-enrichment, with allanite as the main REE mineral (Andersson et al., 2006). In central Finland, the c. 1850 Ma Lamujärvi syenites are also enriched in LREE, chiefly hosted in allanite and monazite (Sarapää et al., 2013). Granites and granitic pegmatites of similar age are known in Sweden and Norway, including the Ytterby pegmatite field in eastern Sweden and the granitoid intrusions of the Transscandinavian Igneous Belt (TIB) which were emplaced in two major phases c. 1810-1770 and 1720-1660 Ma (Romer et al., 1992, Åhäll and Larson, 2000). Most of these intrusions are not considered to contain significant REE mineralization (Müller, 2010). However, an exploration campaign in the Tysfjord granitic complex identified locally elevated REE concentrations in soil (up to c. 1500 ppm total rare earths, Sc and Y excluded; Finne and Eggen (2013)). More regional-scale data are required to determine the REE potential of the most evolved TIB-associated granitoids.

3.3 Mesoproterozoic Rift Systems

Collisional and accretionary tectonics continued to dominate within Fennoscandia and around the margins of the North Atlantic Craton until around 1500 Ma, when localised zones of extension and rifting began to develop in some areas (Bogdanova et al., 2008). Extensional tectonics became dominant after 1400 Ma, and eventually led to the break-up of the supercontinent of Columbia around 1200 Ma (Zhao et al., 2004). These extensional rifts represent significant belts of REE mineralisation in northern Europe.

In Sweden, a major roughly north-south zone of weakness known as the Protogine Zone developed in the Mesoproterozoic and was reactivated numerous times, with repeated magmatic episodes (Andréasson and Rodhe, 1990, Söderlund and Ask, 2006). To either side of this zone, voluminous rapakivi granite magmatism gave way to a phase of bimodal mafic-felsic, syn-tectonic, intracratonic magmatism at c. 1470-1440 Ma (Brander and Söderlund, 2009). Geochemically, the felsic part of this magmatic suite has features of A-type granites, such as moderate enrichment in the REE (Cecys and Benn, 2007). This A-type suite includes some small bodies of peralkaline syenite with elevated REE contents, most notably the Norra Kärr Alkaline Complex in southern Sweden, emplaced at 1489 ± 8

Ma (Sjöqvist et al., 2013). Norra Kärr is a body of deformed, agpaitic, peralkaline nepheline syenite, about 1300 x 400 m in size, which is rich in eudialyte-group minerals and their alteration products such as catapleiite (Sjöqvist et al., 2013). It has an NI-43-101 compliant indicated resource of 41.6 million tonnes (Mt) at 0.57% TREO, and an inferred resource of 16.5 Mt at 0.64% TREO (using a TREO cut-off of 0.17%) (Gates et al., 2013). The Almunge nepheline syenite in Sweden has been considered to be of similar age (Doig, 1970), but recent dating suggests that it is Palaeoproterozoic in age and unrelated to the magmatism at Norra Kärr (Delin and Bastani, 2009).

The Gardar Province of South Greenland is a Mesoproterozoic rift zone that developed along the southern margin of the Archaean North Atlantic Craton during two separate periods of activity, c. 1280-1250 Ma and 1180-1140 Ma (Upton and Emeleus, 1987, Upton et al., 2003, Upton, 2013). Both Gardar rifting events include volcanic rocks, large volumes of mafic dykes, major plutons of silica-saturated and silica-undersaturated syenite and peralkaline granite, and minor carbonatite bodies. Alkaline magmatism of similar age extends into Canada (e.g. Strange Lake, Miller et al. (1997)) and possibly into Sweden (e.g. the Kalix-Storö dykes, Kresten et al. (1981)), thus indicating a wide network of rift zones and alkaline magmatism associated with the break-up of Columbia. To date, the Gardar Province is considered to represent the most important area of REE resources in Europe.

The most well-known REE deposits in the Gardar Province lie within the Ilímaussaq Complex (Figure 6), a major layered granitic-syenitic intrusive complex (18 km x 8 km) with a significant component of peralkaline, agpaitic nepheline syenite (Larsen and Sørensen, 1987, Markl et al., 2001). The complex has been dated at 1160 ± 5 Ma (Krumrei et al., 2006), and is thus one of the younger intrusions within the Gardar Province. It has been affected by later faulting with downthrow to the north, such that both the roof and the lower parts of the magma chamber can be studied. The complex was formed by successive intrusions of increasingly differentiated alkaline melts; early augite syenites form the margins of the complex, and are locally intruded by sheets of quartz syenite and alkali granite. These were subsequently intruded by one or more pulses of agpaitic magma, forming the layered nepheline syenites in the main core of the complex (Markl et al., 2001, Sørensen, 2006, Pfaff et al., 2008). The extreme and unusual compositions of the agpaitic magma at Ilímaussaq produced a number of rare minerals, many of which are enriched in REE (Sørensen, 1992). Exploration interest has focused on the agpaitic nepheline syenites, notably the lower c. 300 m of spectacular layered kakortokites (eudialyte-arfvdedsonite-nepheline syenites), and the overlying c. 500 m of lujavrite (melanocratic, eudialyte- or steenstrupine-bearing nepheline syenite).

Ilímaussaq hosts two separate REE exploration projects, Kringlerne and Kvanefjeld (Thrane et al., 2014). The Kringlerne deposit comprises the layered kakortokites in the southern part of the IlÍmaussaq Complex, with eudialyte-group minerals and their alteration products (notably catapleiite and nacareniobsite-(Ce)) (Borst et al., in press) as the main economic minerals. Although formal resource information has not been published, estimates suggest the possibility of inferred resources of at least 4,300 Mt grading 0.65% TREO, 0.2% Nb_2O_5 and 1.8% Zr_2O_5 (Thrane et al., 2014).

The Kvanefjeld deposit lies in the northern part of the Ilímaussaq Complex. The main ore rocks are fine-grained lujavrites that are considered to have formed from highly fractionated, volatile-rich agpaitic magmas emplaced in fracture systems beneath the solid roof of the magma chamber (Sørensen et al., 2011). Steenstrupine is the main REE ore mineral in this lithology. A JORC-compliant estimate for Kvanefjeld suggests indicated REE resources of 437 Mt grading 1.1% TREO (Thrane et al., 2014). The deposit also contains economic concentrations of uranium, mainly in steenstrupine, and zinc in sphalerite.

The Gardar Province contains several other syenite complexes that have the potential for REE resources; the most important of these is the Igaliko Complex, which contains four separate intrusive centres. One of these, the Motzfeldt centre, has been known for some time to host Th-U-Nb-Ta-Zr-REE mineralisation (Tukiainen, 1988). The Motzfeldt centre (1273 ± 6 Ma (McCreath et al., 2012)) is made up of multiple intrusions of nepheline syenite, the majority of which are miaskitic. However, the mineralisation is associated with the latest intrusive phase, comprising agpaitic peralkaline sheets that cut hydrothermally altered nepheline syenites, largely around the margins of the centre. Metasomatic alteration in older syenites was related to these latest, highly-fractionated agpaitic magmas (McCreath et al., 2012). The potential resources of REE and HFSE are thus hosted both in the altered syenites and in the peralkaline sheets themselves. Ore minerals include pyrochlore, columbite, bastnäsite, monazite, eudialyte-group minerals and zircon. Current estimates suggest an exploration potential in one area of altered syenites (the Aries Prospect) of 200-500 Mt grading 0.3-0.5% TREO, 0.18-0.22% Nb_2O_5, and 0.013-0.016% Ta_2O_5 (Tukiainen, 2014). Further resources are likely to exist in other outcrop areas of peralkaline sheets within the complex, particularly in North and South-east Motzfeldt (Tukiainen, 2014).

The North Qôroq Centre of the Igaliko Complex has many similarities to the Motzfeldt Centre, being made up of several nepheline syenite intrusions of which the latest are agpaitic and contain significant proportions of eudialyte-group minerals (Coulson and Chambers, 1996, Coulson, 2003). As at Motzfeldt, metasomatic alteration of older syenites is extensive, with evidence of REE mobilisation and formation of REE-fluorcarbonate minerals such as synchysite, parisite and bastnäsite (Coulson and Chambers, 1996). There is thus potential for recognition of REE resources in North Qôroq. Agpaitic compositions have not been recognised in the other centres of the Igaliko Complex, or indeed elsewhere in the Gardar Province.

Peralkaline granites are minor constituents of the Gardar Province, the most famous being the Ivigtut granite, which was host to the world's most important cryolite deposit (now largely mined out). This granite stock was strongly affected by metasomatic alteration and REE remobilisation during formation of the cryolite deposit (Goodenough et al., 2000, Köhler et al., 2008) but there has been no detailed study of REE minerals and areas of REE enrichment. Carbonatites are also known within the Gardar Province, particularly at Grønnedal-Ika (Pearce et al., 1997) and Qassiarsuk (Andersen, 1997). These carbonatites typically show enrichment in the LREE (Coulson et al., 2003) but have not been explored in detail.

3.4 Neoproterozoic orogenic belts and rift systems in northern Europe

From around 1100 Ma, accretionary and collisional tectonics again began to dominate in Europe as the supercontinent of Rodinia was assembled, forming the Grenville and Sveconorwegian orogenic belts (Li et al., 2008). The Sveconorwegian lacks the hydrothermal REE deposits of the Svecofennian. However, local enrichment of REE occurs in numerous pegmatites of the Sveconorwegian pegmatite province (900 to 1100 Ma) extending from SW Sweden to SW Norway, and including the Evje-Iveland, Froland and Glamsland pegmatite fields (Romer and Smeds, 1996, Müller et al., 2008). The most common REE minerals in these pegmatites are allanite, monazite, aeschynite, fergusonite and gadolinite. Generally, these deposits are either too small or too low in grade to be commercially exploited solely for REE, but REE could potentially be by-products of feldspar and/or quartz mines, such as the Glamsland mine which closed in 2009.

After c. 850 Ma, Rodinia began to break up, with the development of continental rifts and eventual formation of the Iapetus Ocean. Some important European REE resources were formed towards the end of the Neoproterozoic, with emplacement of carbonatites and lamprophyres distributed around the North Atlantic Craton and Fennoscandian Shield, together with some more extensive areas of alkaline magmatism. These are part of the Central Iapetus Magmatic Province (Ernst and Bell, 2010) which developed on the Laurentian and Baltican margins of the newly-forming Iapetus Ocean. Siting of these individual intrusive bodies is likely to have been controlled by crustal-scale structures that provided magma pathways, but it is unclear whether the magma sources can be attributed to a plume or to extension in a number of separate rifts.

In West Greenland, the Sarfartoq carbonatite, together with associated kimberlitic and lamprophyric minor intrusions, were emplaced into Archaean rocks at the margin of the North Atlantic Craton at c. 565 Ma (Hutchison and Heaman, 2008, Secher et al., 2009). The carbonatite is made up of a c. 10 km^2 core series of concentric dolomite carbonatite sheets, surrounded by a marginal zone with carbonatite dykes cutting highly altered (fenitised) Archaean gneisses. The REE are concentrated in shear zones and pyrochlore-rich veins within the marginal zone (Secher and Larsen, 1980). The main REE minerals are synchysite-(Ce), synchysite-(Nd), bastnäsite-(Ce) and monazite-(Ce) (Tuer, 2011). The Sarfartoq intrusion has a NI 43-101-compliant resource estimate including indicated resources of 5.9 Mt grading 1.8% TREO, and inferred resources of 2.5 Mt grading 1.6% TREO (using a TREO cut-off of 1%) (Tuer, 2012).

In Norway, the Fen carbonatite was emplaced into Mesoproterozoic orthogneisses at c. 580 Ma (Meert et al., 1998). It forms a subcircular body of c. 9 km^2 at the surface, and includes a variety of carbonatite types: pyroxene- and amphibole-bearing sövite (calcite carbonatite), dolomite carbonatite, ankerite ferrocarbonatite and haematite carbonatite, as well as minor intrusions of nepheline syenite (Andersen, 1988). The gneisses around the complex have been intensely altered by alkaline metasomatic fluids, giving rise to the term ‘fenitisation’. Highest REE contents are found in the ferrocarbonatite and haematite carbonatite, which are LREE-enriched; the main REE-bearing minerals are monazite, bastnäsite, parisite and apatite (Andersen, 1986). The carbonatites have previously been mined for iron ore and subsequently for Nb at the Søve mine, and have more recently been considered for their resources of REE, Th and apatite (Ihlen et al., 2014). In the south and east of the complex, an inferred resource of 84 Mt grading 1.08% TREO (0.8% TREO cut-off) has been outlined (Lie and Østergaard, 2014), but the resources in the complex as a whole are likely to be greater.

In Sweden, the Alnö carbonatite complex was emplaced contemporaneously with the Fen carbonatite, at c. 585 Ma (Meert et al., 2007, Rukhlov and Bell, 2010). It comprises a number of intrusive centres, including the main carbonatite-syenite-ijolite-pyroxenite centre on Alnö Island, a smaller centre on the mainland at Söråker, and a swarm of carbonatite dykes (Morogan and Woolley, 1988). Fenitisation is extensive around most of the intrusions, and the fenites are typically enriched in LREE over HREE (Morogan, 1989). REE contents are highest in the carbonatitic rocks, and specifically in the sövites (Hornig-Kjarsgaard, 1998). The carbonatites include a wide range of REE-bearing minerals such as apatite, monazite, titanite, pyrochlore, bastnäsite and synchysite, but except for some recent activity in the Söråker area, there has been no formal exploration within the complex.

A major area of latest Neoproterozoic alkaline and carbonatitic igneous rocks is the Seiland Igneous Province, which occurs in the allocthonous Caledonian nappes of northern Norway. The most voluminous parts of the province comprise sub-alkaline to mildly alkaline gabbroic rocks, but the latest intrusions include syenites, nepheline syenites and carbonatites dated at 580-560 Ma (Roberts et al., 2010). REE enrichments have not been identified in the area (Ihlen et al., 2014) but there may be potential for exploration.

3.5 Cambrian to Silurian rift systems and sedimentary basins

Neoproterozoic continental rifting in northern Europe was largely terminated by the transition to drift and the opening of the Iapetus Ocean. Within Europe, the main locus of continental rifting shifted southward, with rifts developing in the northern part of Gondwana during the Cambrian. These rifts would eventually lead to opening of the Rheic Ocean during the Ordovician (Nance et al., 2010). Magmatism associated with this period of rifting is now well-preserved in the Bohemian Massif (Pin et al., 2007) and in the Iberian massif of Spain and Portugal (Sánchez-García et al., 2010). The main rift-related sequence in the Iberian massif is dominated by volcanic rocks with some plutons, typically sub-alkaline to alkaline in nature (Sánchez-García et al., 2003). These include a large area of peralkaline granitoids, the 482 ± 2 Ma Galiñeiro Complex (Montero et al., 2009). This complex has notable enrichments in the REE, hosted in a range of minerals including allanite, monazite, xenotime, zircon, bastnäsite, thorite and REE niobotantalates (aeschynite, fergusonite, samarskite and pyrochlore group minerals) (Montero et al., 1998).

An unusual suite of REE-enriched rocks exists in the form of authigenic nodular monazite layers in Palaeozoic sedimentary basins across western and central Europe. Such monazite nodules are found in Lower Palaeozoic turbidite sequences in Central Wales and in Belgium, and are considered to have formed by REE remobilisation during diagenesis (Burnotte et al., 1989, Milodowski and Zalasiewicz, 1991). They are typically characterised by cores that show enrichment in the middle REE with LREE-enriched rims, and are lower in Th than igneous monazites (Milodowski and Zalasiewicz, 1991). In Brittany, similar monazite nodules have locally been eroded from their host sedimentary rocks and concentrated into alluvial placers (Donnot et al., 1973). These monazites similarly show MREE-enriched cores and LREE-enriched rims (Tuduri et al., 2013). Within the Iberian massif, REE enrichments are found in Ordovician quartzites in Vale de Cavalos in Portugal (de Oliveira, 1998). The REE are hosted in detrital minerals such as zircon and rutile, and also in nodular monazite.

3.6 Silurian post-collisional magmatism: the Caledonian Belt

During the Silurian, closure of the Iapetus Ocean and collision between Laurentia, Baltica and Avalonia formed the Caledonide orogenic belt which extends through northern Germany, Norway, the northern British Isles, and east Greenland, and into the Appalachians of North America (McKerrow et al., 2000). Parts of the Caledonian belt are marked by voluminous syn- to post-collisional calc-alkaline to alkaline magmatism (Atherton and Ghani, 2002) with localised areas of more highly alkaline magmatism.

In northern Scotland, a suite of high-K syenitic to pyroxenitic plutons was emplaced at 431-425 Ma (Goodenough et al., 2011). Of these, the most significant REE enrichments are found in the Loch Loyal Complex (Hughes et al., 2013), where allanite-rich mafic syenites have been affected by late-stage hydrothermal alteration that has concentrated the REE into biotite-magnetite-rich veins with up to 2% TREO (Walters et al., 2013). The main REE-bearing minerals are allanite, apatite, titanite and REE-carbonate (Walters et al., 2013). In Norway, the Misværdal Complex (c. 440 Ma) also comprises high-K intrusions of pyroxenite and granitoid, intruded into the Caledonian belt. The pyroxenites show local enrichments in allanite and apatite, with significant REE contents (Ihlen et al., 2014). Similar high-K magmatism also occurs in east Greenland, with examples in the Batbjerg Complex (Brooks et al., 1981) and in Milne Land (Kalsbeek et al., 2008). In Milne Land, heavy minerals have been eroded from the plutons and subsequently concentrated in Jurassic placer deposits (Larsen et al., 2003) that are of interest for their REE enrichment. In Jämtland, Sweden, nepheline syenites and carbonatitic rocks occur within the Caledonide nappes. These rocks contain REE hosted by pyrochlore-group minerals and bastnäsite (Jonsson and Stephens, 2004). Recent exploration in the area has so far failed to find any evidence for larger carbonatitic bodies.

3.7 Devonian to Permian rifting and Variscan belts

During the Devonian and Carboniferous, much of central and southern Europe was affected by Variscan orogenesis associated with the closure of the Rheic Ocean, whilst rifting and alkaline magmatism developed in the foreland to the Variscan (Timmerman, 2004). Pronounced continental rifting in the Baltic Shield at 390-360 Ma led to the formation of the Kola Alkaline Province, one of the most well-studied areas of alkaline magmatism in the world (Arzamastsev et al., 2001, Downes et al., 2005, Kogarko et al., 2010). During the early Carboniferous, around 350 Ma, a phase of rifting affected the British Isles, Norway, and into north Germany and Poland. Minor alkaline magmatism also developed during the Carboniferous in a post-collisional setting within the Variscan orogenic belt, notably in the Bohemian massif. Subsequently, an extensive rift system developed to the north of the Variscan orogenic belt through the late Carboniferous and early Permian (Wilson et al., 2004). These continental rifts represent notable areas of alkaline magmatism with significant potential for REE deposits.

The majority of the Kola Alkaline Province lies in Russia, where it contains significant REE deposits in the Khibiny and Lovozero intrusive complexes (Kogarko et al., 2010), but is outside the geographical scope of this paper. The westernmost part of the province falls within the Finnish border, with two main intrusions: the Sokli phoscorite-carbonatite complex, and the Iivaara alkaline complex. Sokli was emplaced at c. 380 Ma (Rukhlov and Bell, 2010) into Archaean gneisses, and covers an area of c. 20 km^2. It has a magmatic carbonatite-phoscorite core in which several intrusive phases can be identified, surrounded by an aureole of fenitised gneiss and pyroxenite (Vartiainen and Paarma, 1979, Lee et al., 2006). The earlier intrusions within the carbonatite comprise calcite carbonatite and phoscorite, with abundant pyrochlore in the phoscorites. Late-stage dykes of dolomite carbonatite cut the earlier intrusions and the fenites, and contain apatite and monazite together with Sr-Ba-LREE-bearing carbonates such as strontianite, alstonite, bastnäsite-(Ce) and ancylite-(Ce) (Lee et al., 2006, Sarapää et al., 2013). Analysis of these veins has indicated TREE contents up to 1.83% (Al-Ani and Sarapää, 2013). The Iivaara alkaline complex is a c. 9 km^2 plug of ijolitic rocks surrounded by a zone of fenitised gneisses (Sindern and Kramm, 2000). Although some apatite and allanite are present in samples from the plug, REE contents are relatively low (Sarapää et al., 2013).

Early Carboniferous magmatism in the Variscan foreland is well known from the British Isles, particularly the Midland Valley and Northern England, where it largely comprises mafic volcanic rocks (Timmerman, 2004). In Poland, geophysical investigations and drilling have revealed a buried alkaline plutonic province of Early Carboniferous age (354-345 Ma) which includes the Pisz and Elk gabbroic to syenitic plutons, and the Tajno pyroxenite-carbonatite-syenite body (Demaiffe et al., 2013). The late carbonatite veins in the Tajno body show LREE enrichment (Demaiffe et al., 2005).

Late-stage alkaline post-collisional magmatism occurred in many parts of the Variscan belt, and can be considered as analogous to the similar magmatism in the Caledonian belt described above. Although alkaline intrusions represent only a small percentage by volume of the voluminous Variscan batholiths that extend across central Europe, there has been limited study of their REE potential. The Bohemian Massif in the Czech Republic hosts ultrapotassic syenitic plutons such as the c. 335-340 Ma Třebíč Pluton (Kotková et al., 2010, Kusiak et al., 2010) which are cut by fields of late, REE-enriched pegmatites with a range of REE minerals including allanite, bastnäsite and euxenite (Škoda and Novák, 2007). Late-Variscan A-type microgranite dykes have also been recognised from the Krušné hory mountains; they show HREE enrichment and contain minerals such as monazite, thorite, xenotime, and pyrochlore (Breiter, 2012).

Widespread rift-related magmatism developed in the British Isles, in the Oslo Rift in Norway, in southern Sweden, and in the North German Basin during the late Carboniferous and into the early Permian (Neumann et al., 2004). Much of this magmatism is still preserved as lava flows, dykes and sills at the surface, such that the plutons that might contain REE resources remain buried. One of the most important areas of alkaline magmatism of this age is the Oslo Rift, which has been subdivided into six stages of rifting and magmatism from c. 300 Ma to c. 240 Ma (Neumann et al., 1992, Larsen et al., 2008, Corfu and Dahlgren, 2008). Lavas are extensive within the rift, and are intruded by a number of alkaline plutons of varying composition. The plutons are dominated by monzonitic compositions and many have marginal pyroxenite bodies, such as the Kodal apatite deposit, which consists of a 1900 m-long zone of closely-spaced pyroxenite lenses within the monzonitic Larvik Plutonic Complex (Ihlen et al., 2014). This deposit is currently being explored for phosphate and Fe-Ti, but has also been recorded as having high REE contents in apatite (Ihlen et al., 2014). Syenitic pegmatites, of both miaskitic and agpaitic type, are also recorded throughout the Larvik Plutonic Complex and may contain REE-bearing minerals (Andersen et al., 2010). Other magmatic bodies that may be of interest for the REE include Sæteråsen in Norway, a Nb-REE mineralisation hosted in a trachytic lava flow (Ihlen, 1983), and Särna in Sweden.

3.8 Mesozoic rifts: Alpine Tethys and Atlantic

Rifting continued throughout Europe during the Mesozoic and into the Cenozoic, with varying amounts of associated magmatism. In western Europe, Atlantic rifting generated the voluminous Central Atlantic Magmatic Province and subsequently the North Atlantic Igneous Province, whereas rifting of the Alpine Tethys in southern and eastern Europe appears to have been associated with rather limited magmatic activity (Stampfli, 2000).

Alpine Tethyan rifting during the Triassic generated alkaline magmatism in the Carpathians, which is still relatively little-known. The most notable REE mineralisation is associated with the c. 230 Ma Ditrău Alkaline Complex in the Eastern Carpathians of Romania (Dallmeyer et al., 1997, Morogan et al., 2000, Fall et al., 2007). REE-rich mineral veins are found within the alkaline complex at Jolotca, and outside the complex at Belcina. The REE mineralised veins include monazite-(Ce), xenotime-(Y), allanite-(Ce), apatite, bastnäsite, parisite, synchysite, fergusonite, polycrase and aeschynite in association with sulphides, carbonates and a wide range of other minerals (Hirtopanu et al., 2010). Disseminated enrichments in REE, Nb and Zr are also found within the roof zone of the alkaline complex in the Lazarea area. A small Triassic alkaline intrusive body associated with REE mineralisation has also been identified in the Slovakian Carpathians (Ondrejka et al., 2007). This area may well have significant potential for discovery of further REE mineralisation.

In contrast, rifting of the Atlantic led to the development of voluminous magmatism. The Central Atlantic Magmatic Province, associated with rifting of the Pangaea supercontinent and formation of the central Atlantic ocean, comprises extensive flood basalts erupted around the Triassic-Jurassic boundary at c. 200 Ma (Marzoli et al., 1999, Blackburn et al., 2013). As the ocean opened, subsequent late Cretaceous rifting cycles (100-70 Ma) emplaced alkaline magmas within the Iberian massif in Spain and Portugal and also in the Pyrenees (Solé et al., 2003, Miranda et al., 2009). REE mineralisation is not currently known in association with this alkaline magmatic phase.

During the Jurassic, continental extension began to develop northwards, marked in Europe by the emplacement of carbonatites and lamprophyres in west Greenland at 165-145 Ma (Secher et al., 2009, Tappe et al., 2009). Both the Qaqarssuk (Qeqertaasaq) and Tikiusaaq carbonatite intrusions are enriched in LREE. The Qaqarssuk carbonatite comprises a series of calcite- and dolomite-carbonatite and silicocarbonatite ring-dykes (Knudsen, 1991) with late-stage sheets of calcite- and ferro-carbonatite that show significant REE enrichment. The major REE minerals are ancylite, burbankite, huanghoite and qaqarssukite (Thrane et al., 2014). The Tikiusaaq carbonatite similarly comprises calcite- and dolomite-carbonatites with later ferrocarbonatite dykes (Tappe et al., 2009). Both carbonatites are surrounded by zones in which the country rock has been fenitised.

Rifting and ocean opening, together with impingement of the Iceland plume, led to development of tholeiitic flood basalt magmatism of the North Atlantic Igneous Province during the Cenozoic, beginning at 62 Ma (Saunders et al., 2013). In East Greenland, the alkaline Gardiner Complex formed at c. 55 Ma (Tegner et al., 2008). It comprises ultramafic cumulates with syenites and carbonatite sheets (Nielsen, 1980) and may have potential for REE mineralisation, although it is extremely difficult to access. On the other margin of the Atlantic, in Scotland and Northern Ireland, REE minerals including chevkinite-group minerals, fergusonite, gadolinite, allanite and monazite have been reported from Cenozoic granites in Arran, Skye and the Mourne Mountains (Hyslop et al., 1999, Moles and Tindle, 2011, Macdonald et al., 2013). However, the bulk compositions of the granites do not exhibit significant REE enrichment.

3.9 Cretaceous to Cenozoic circum-Mediterranean rifts

Intraplate, extensional magmatism has been common through much of Europe during the Cenozoic, particularly in areas of Variscan basement around the Alpine collisional zone

(Wilson and Downes, 2006). To the north of the Alps, alkaline volcanism developed in the Rhenish Massif and Rhine Graben in Germany, the Massif Central in France, and the Bohemian Massif in the Czech Republic. To the south and east, subduction-related magmatism was followed by more alkaline volcanism in Italy, Greece, Turkey and parts of Eastern Europe such as the Pannonian Basin (Agostini et al., 2007). In all of these areas, the current surface expression of the magmatism constitutes volcanic fields and their eruptive products, most commonly basanitic and basaltic (Wilson and Downes, 2006). Carbonatitic magmas are rare, but locally present. It seems highly likely that plutons with potential for REE enrichment may exist beneath these areas.

In eastern Germany, the Delitzsch carbonatite-lamprophyre complex lies buried beneath c. 100 m of Cenozoic sediments. It was discovered during exploration for uranium deposits in the 1960s and 1970s. Extensive drilling has proved lamprophyres and carbonatite dykes and plugs down to c. 1100m, across an area of c. 450 km^2 (Krűger et al., 2013). The presence of xenoliths of coarse carbonatite in diatreme breccias is considered to indicate a carbonatitic pluton at greater depths (Seifert et al., 2000). REE minerals in the carbonatites include apatite, pyrochlore and bastnäsite. One of the carbonatitic diatremes, the Storkwitz diatreme, has estimated total (indicated and inferred) resources of 4.4 Mt @ 0.45% TREO (Deutsche-Rohstoff, 2013). Recent dating (Krűger et al., 2013) suggests an emplacement age for the complex of 75-71 Ma, indicating early reactivation of Variscan structures in the Alpine foreland.

One of the more well-known carbonatites of this age is the Miocene Kaiserstuhl Volcanic Complex (Keller, 1981, Kraml et al., 2006, Wang et al., 2014) in the Rhine Graben. It comprises volcanic rocks and dykes of alkaline silicate composition, as well as carbonatitic dykes, intrusions and diatreme breccias. The carbonatites show significant REE enrichment (Hornig-Kjarsgaard, 1998) and hydrothermal alteration of phonolites has generated an economic zeolite deposit which contains the rare earth-bearing phase götzenite (Weisenberger et al., 2014). It seems likely that plutonic rocks of interest for their REE concentrations may be present beneath Kaiserstuhl.

In southern Europe, extrusive carbonatites occur in association with alkaline to peralkaline volcanic rocks at a number of localities in Italy, including San Venanzo, Polino and Cupaello in the Intra-Montane Ultra-alkaline province, and the Monte Vulture volcanic complex (Stoppa and Woolley, 1997, Downes et al., 2002). In these areas, compressional tectonics associated with Apennine folding and thrusting have passed into an extensional regime over the last 5 Ma (Lavecchia and Boncio, 2000). The presence of coarse-grained carbonatite tephra at Monte Vulture indicates that intrusive carbonatites are present at depth, and these rocks are enriched in the LREE as is typical of carbonatites (Rosatelli et al., 2000, Mongelli et al., 2013). Beach sands along the Italian coastline, particularly at Nettuno near Rome, contain REE minerals such as perrierite-(Ce) that may be derived from the alkaline volcanics (Macdonald et al., 2009).

In Greece, alkaline volcanic rocks are known from many localities in the Aegean (Agostini et al., 2007). However, the most important REE concentrations are not associated with alkaline rocks, but are found in heavy mineral sands on the coast in the Nea Peramos and Strymonikos Gulf areas. REE-bearing minerals in these placers include monazite, allanite, titanite, uraninite, zircon and apatite (Eliopoulos et al., 2014). Geochemical and mineralogical studies indicate that these minerals are derived from the Symvolon and Kavala plutons, which are deformed granodioritic complexes of Miocene age (Dinter et al., 1995).

Alkaline igneous rocks and carbonatites of Cretaceous to Cenozoic age are common in the Anatolian rift systems in Turkey, and would deserve further work to understand their potential for REE mineralisation. Of particular significance is the c. 25 Ma Kizilcaören Complex, which comprises phonolite and trachyte stocks, carbonatite dykes, and a fluorite-barite-LREE deposit forming veins and breccias fillings in the Palaeozoic country rock (Gültekin et al., 2003, Nikiforov et al., 2014). The ore assemblage contains barite, fluorite, quartz, calcite, feldspar and phlogopite, with bastnäsite as the main REE mineral accompanied by brockite, fluocerite, monazite and parisite (Gültekin et al., 2003, Nikiforov et al., 2014). The mineralisation can be related to hydrothermal activity associated with the alkaline magmatism. Late Cretaceous syenites with associated carbonatites and fluorite mineralisation have been described from east-central Anatolia, including the Karaçayir pluton (Cooper et al., 2011) and the area around Malatya, which contains the Sofular carbonatite (Ozgenc, 1999, Ozgenc and Ilbeyli, 2009). The Quaternary alkaline volcanism of Gölcűk, close to Isparta in south-western Turkey, shows enrichment in the REE (Platevoet et al., 2014) and has been proposed as a possible source for heavy minerals in the nearby Çanakli placer (Aksu Diamas REE prospect).

3.10 Bauxites

Bauxite deposits occur along the northern shore of the Mediterranean Sea (Figure 7), from Spain to Turkey, encompassing parts of southern France, Hungary, Italy, Greece and the Balkans (Bárdossy, 1982, Özlü, 1983). Many of these bauxites, which formed by intense lateritic weathering of residual clays, are currently mined for aluminium, and the red mud waste from bauxite processing represents a potential REE resource (Deady et al., 2014). A pioneer study described the existence of authigenic REE-bearing minerals within karst bauxites of the San Giovanni Rotondo deposit, in Italy (Bárdossy and Panto, 1973). The presence of REE-bearing minerals within bauxites was confirmed by Bárdossy et al. (1976) for the Nagyharsány deposit, in Hungary and subsequently for a range of other deposits (Maksimovic and Panto, 1996). The most abundant REE-bearing minerals are members of the bastnäsite group, and the most frequent is hydroxylbastnäsite ($REE(CO_3)(OH)$), followed by synchysite-(Nd), bastnäsite-(Ce) and bastnäsite-(Nd). Other minerals described include monazite-(Nd), monazite-(La), Nd-rich goyazite, florencite and crandallite (Maksimovic and Panto, 1996). The REE contained within bauxites pass into red mud wastes after processing, and represent a low-grade but potentially large-tonnage resource of REE in Europe (Deady et al., 2014).

4. Discussion

From the assessment above, it is clear that Europe already has substantial known REE resources, and that there is significant potential for further resources to be recognised. The majority of the known resources, and many potential future exploration areas, are associated with alkaline magmatism and carbonatites developed in intracontinental rift settings. However, REE can be concentrated in other settings, most notably associated with post-collisional alkaline magmas. The REE deposits of the Svecofennian belt are unique in Europe, in that they were formed by hydrothermal processes associated with active subduction. Secondary deposits are also of interest, although typically low-grade; they include diagenetic nodular monazites, sedimentary placers, and deposits formed by weathering such as bauxites. REE-enriched placers in particular are typically found in areas where alkaline magmatism exists nearby, although few REE placers have been studied in any detail.

Many of Europe’s current exploration projects for REE are associated with carbonatites, including Sarfartoq and Qaqarssuk in Greenland, Fen in Norway and Storkwitz in Germany. Many of these have the advantage that they contain the mineral bastnäsite, currently the most commonly processed REE ore mineral (Jordens et al., 2013). However, the majority of carbonatites are strongly enriched in the LREE (Chakhmouradian and Zaitsev, 2012) and have lower contents of the most critical HREE.

Higher contents of the most critical REE are found in deposits where the main REE minerals include xenotime, eudialyte-group minerals, or to a lesser extent monazite (Chakhmouradian and Wall, 2012). Both monazite and xenotime have been mined outside Europe from heavy mineral placers, and processing methods have been established for both minerals (Jordens et al., 2013). These minerals are typically formed in miaskitic igneous rocks and several potential REE deposits of this type are known in Europe, including the xenotime-bearing mineralisation associated with the Galiñeiro and Ditrău complexes. A number of heavy mineral placers formed by erosion of miaskitic plutons also occur within Europe. However, both xenotime and monazite typically contain high levels of Th and U, creating possible issues with radioactive waste (Chakhmouradian and Wall, 2012). Nonetheless, most REE deposits of this type in Europe have been the subject of only limited research, and would deserve much more investigation.

Currently, there is a significant European focus on eudialyte-group minerals and their alteration products as a source of the critical REE, particularly needed in the magnet industry. Ores containing eudialyte-group minerals may have lower REE grades than those bearing monazite and xenotime, but they are also typically characterised by lower Th and U contents. Research into eudialyte-group mineral beneficiation and processing is ongoing as part of the EURARE project, but has not been successfully carried out on a commercial scale. Europe has resources of eudialyte-group minerals in Norra Kärr and in the intrusions of the Gardar Province, particularly Ilímaussaq; other significant agpaitic intrusions are not known at the present time, but may remain to be discovered.

Europe has a wide variety of REE deposits and it is very likely that many more remain to be discovered. A key point that emerges from this review is the existence of ‘fertile zones’ for REE mineralisation. The stable cratonic areas in Greenland and Scandinavia have only limited evidence of alkaline magmatism despite their long histories, but many of Europe’s carbonatites are focused along craton margins. Surrounding these cratons are the more fertile zones, which have initially been affected by subduction in accretionary orogens, potentially fertilising the lithospheric mantle. Subsequently, in many cases hundreds of millions of years later, reactivation of these areas by extensional tectonics has led to alkaline igneous activity and enrichment in REE. A clear example of this comes from Southern Greenland, where Gardar Province magmas were derived from lithospheric mantle that was metasomatised and fertilised some 600 million years earlier during subduction and formation of the Ketilidian belt (Goodenough et al., 2002). In Norway, the Fen carbonatite and associated dyke swarms, and the subsequent Oslo Rift, represent two episodes of alkaline magmatism (Dahlgren, 1994) localised along the margin of a Neoproterozoic subduction-related igneous province associated with the Sveconorwegian event (Slagstad et al., 2013). Further south in Europe, many areas that were affected by the Variscan orogeny have been reactivated during the Cenozoic, with the emplacement of alkaline magmas. A notable example is the Bohemian Massif, in which Palaeozoic subduction-related magmatism (Schulmann et al., 2009) was followed by post-collisional alkaline magmatism, with subsequent reactivation and formation of a rift-related alkaline igneous province during the Cenozoic (Ulrych et al., 2011). In the Iberian massif, initial alkaline magmatism associated with Rheic Ocean rifting was followed by Variscan collision and then by a further period of alkaline magmatism. In general, areas where Variscan belts have been reactivated by later rifting with alkaline magmatism would appear to be of great interest for REE exploration. To the south of the Alpine mountain chain, there is significant potential for REE enrichments at depth beneath the alkaline volcanic rocks of Italy and Turkey.

5. Conclusions

This overview demonstrates that Europe has a wide range of REE deposits and occurrences. The most significant primary deposits are associated with alkaline igneous rocks and carbonatites formed in extensional settings, although a range of deposits of hydrothermal and igneous origin can be formed in other geodynamic settings. Secondary deposits include placers, which can commonly be linked back to an igneous source, and bauxites in southern Europe.

The most well-known primary deposits are those associated with Mesoproterozoic rift-related magmatism in Greenland and Sweden, and with Neoproterozoic to Palaeozoic carbonatites across Greenland and the Fennoscandian Shield. However, there are a number of less-well known deposits in areas where Europe's Variscan belts have been reactivated by later rifting with the emplacement of alkaline magmas, and these represent important targets for further research. It is clear that Europe has the REE deposits needed to secure its own supply of these elements for the foreseeable future, but that there is a need to develop beneficiation and processing methods in order to ensure sustainable exploitation.

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Figure captions

Figure 1: Schematic diagram to illustrate the main environments of formation of alkaline igneous rocks, major hosts of many REE deposits.

Figure 2: Overview map of Europe showing the approximate extent of the key REE metallogenetic belts described in this paper. Notable REE deposits and occurrences that do not fall within a distinct belt and are not shown on other maps are indicated by symbols.

Figure 3: Simplified geological map of Greenland showing the main REE deposits and occurrences. Base geological map from GEUS.

Figure 4: Simplified geological map of the Scandinavian countries showing the main REE deposits and occurrences. Base geological map after Eilu (2012).

Figure 5: Simplified geological map of Bergslagen, Sweden, showing the location of the main areas of REE deposits and occurrences. Modified after Jonsson et al. (2014).

Figure 6: Geological map of the Ilímaussaq syenite complex showing the location of the main REE deposits after Upton (2013).

Figure 7: Map of the bauxite deposits in the Mediterranean area, after Deady et al. (2014).

Tables

Table 1: Table of all the main REE-bearing minerals and mineral groups found in the European deposits and occurrences described here. Note that many of these groups contain a range of individual mineral species (Wall, 2014), for example the monazite group includes monazite-(La), monazite-(Ce), monazite-(Nd) and monazite-(Sm). For simplicity, these variations are encompassed as REE (LREE/HREE) in the formulae given here. Mineral groups are marked with an asterisk.

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Figure 1

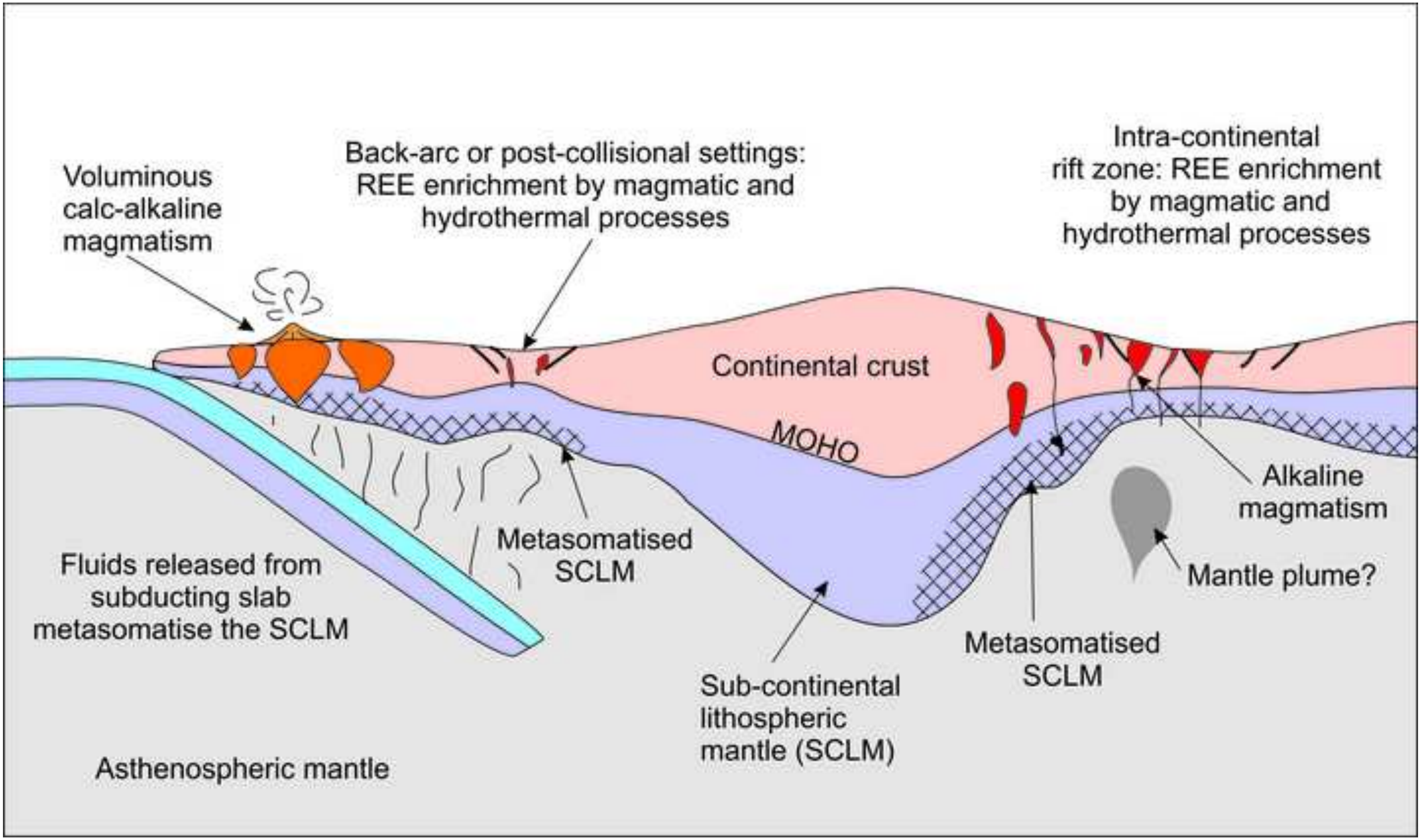

Voluminous
calc-alkaline
magmatism
Back-arc or post-collisional settings:
REE enrichment by magmatic and
hydrothermal processes
Intra-continental
rift zone: REE enrichment
by magmatic and
hydrothermal processes
Continental crust
MOHO
Alkaline
magmatism
Mantle plume?
Metasomatised
SCLM
Metasomatised
SCLM
Fluids released from
subducting slab
metasomatise the SCLM
Sub-continental
lithospheric
mantle (SCLM)
Asthenospheric mantle

Figure 2

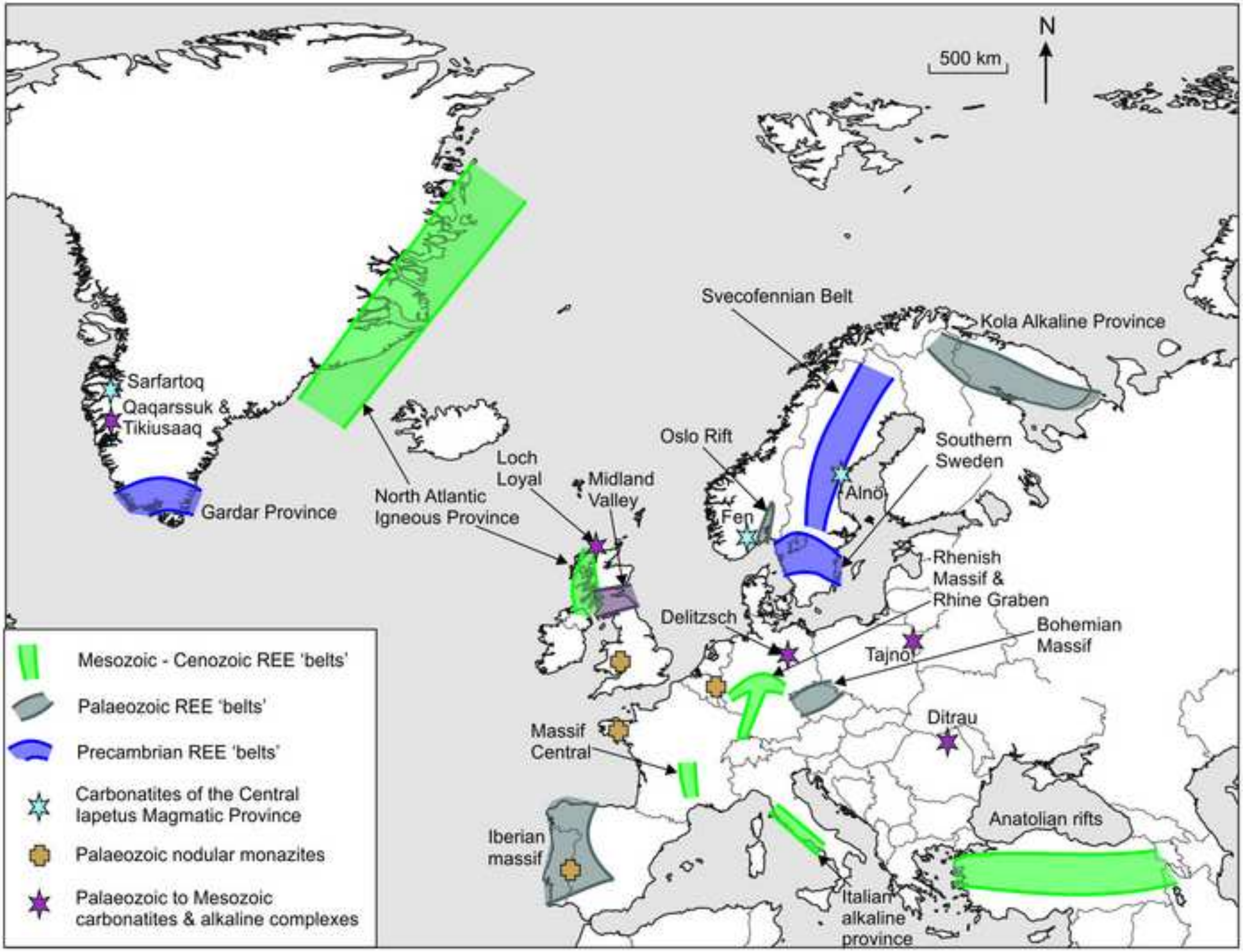
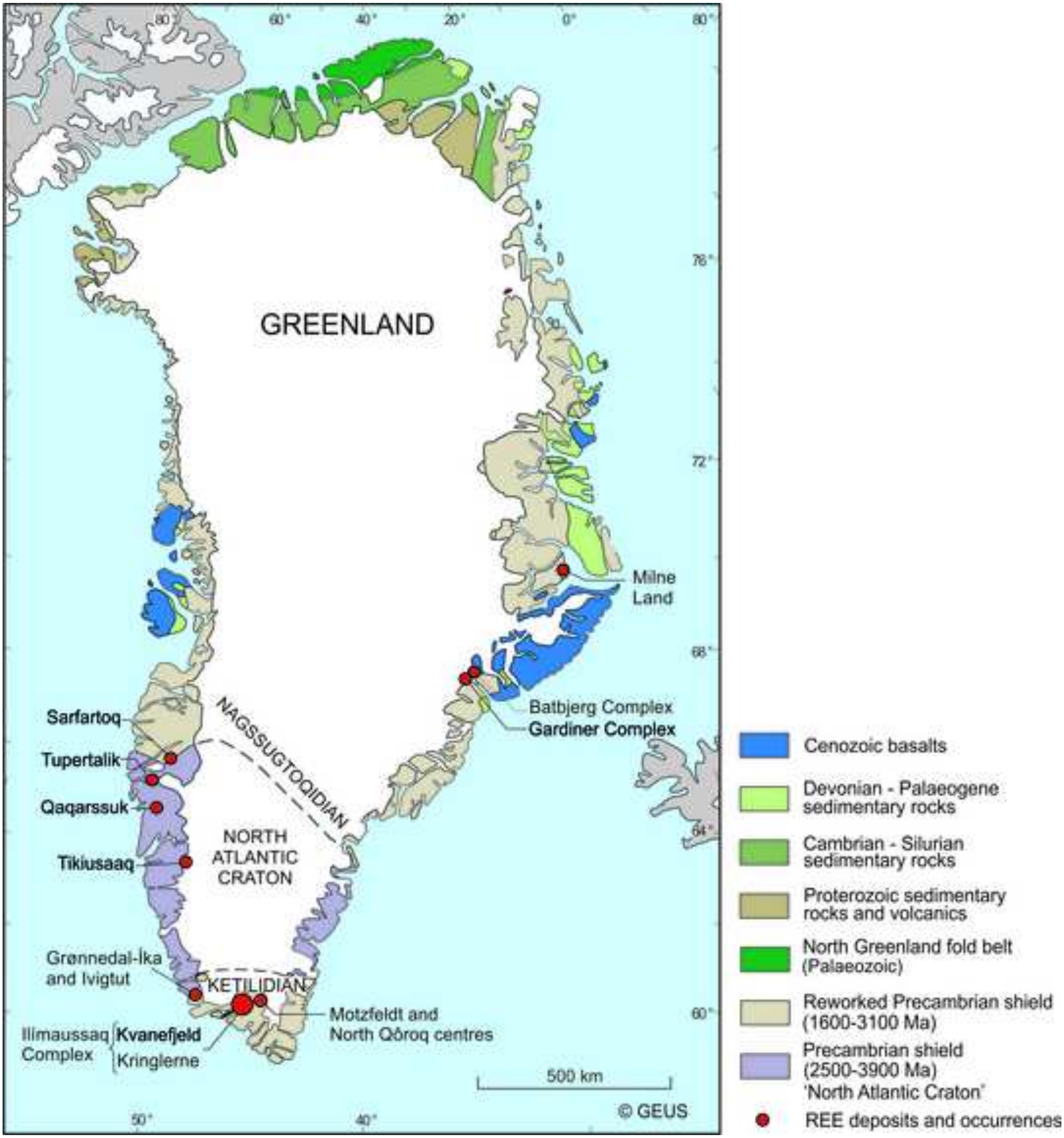

500 km
N
Sarfartoq
Qaqarssuk &
Tikiusaaq
Gardar Province
North Atlantic
Igneous Province
Loch
Loyal
Midland
Valley
Oslo Rift
Fen
Svecofennian Belt
Alnö
Southern
Sweden
Kola Alkaline Province
Rhenish
Massif &
Rhine Graben
Delitzsch
Tajno
Bohemian
Massif
Ditrau
Massif
Central
Iberian
massif
Italian
alkaline
province
Anatolian rifts
Mesozoic - Cenozoic REE 'belts'
Palaeozoic REE 'belts'
Precambrian REE 'belts'
Carbonatites of the Central
Iapetus Magmatic Province
Palaeozoic nodular monazites
Palaeozoic to Mesozoic
carbonatites & alkaline complexes

Figure 3


GREENLAND
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40°
20°
0°
80°
76°
72°
68°
64°
60°
50°
40°
Milne Land
Batbjerg Complex
Gardiner Complex
NAGSSUGTOQIDIAN
NORTH ATLANTIC CRATON
Sarfartoq
Tupertalik
Qaqarssuk
Tikiusaaq
Grønnedal-Íka and Ivigtut
KETILIDIAN
Motzfeldt and North Qôroq centres
Ilímaussaq Complex
Kvanefjeld
Kringlerne
500 km
© GEUS
🟦 Cenozoic basalts
🟩 Devonian - Palaeogene sedimentary rocks
🟩 Cambrian - Silurian sedimentary rocks
▨ Proterozoic sedimentary rocks and volcanics
🟩 North Greenland fold belt (Palaeozoic)
▨ Reworked Precambrian shield (1600-3100 Ma)
🟪 Precambrian shield (2500-3900 Ma) 'North Atlantic Craton'
● REE deposits and occurrences

Figure 4
Click here to download high resolution image

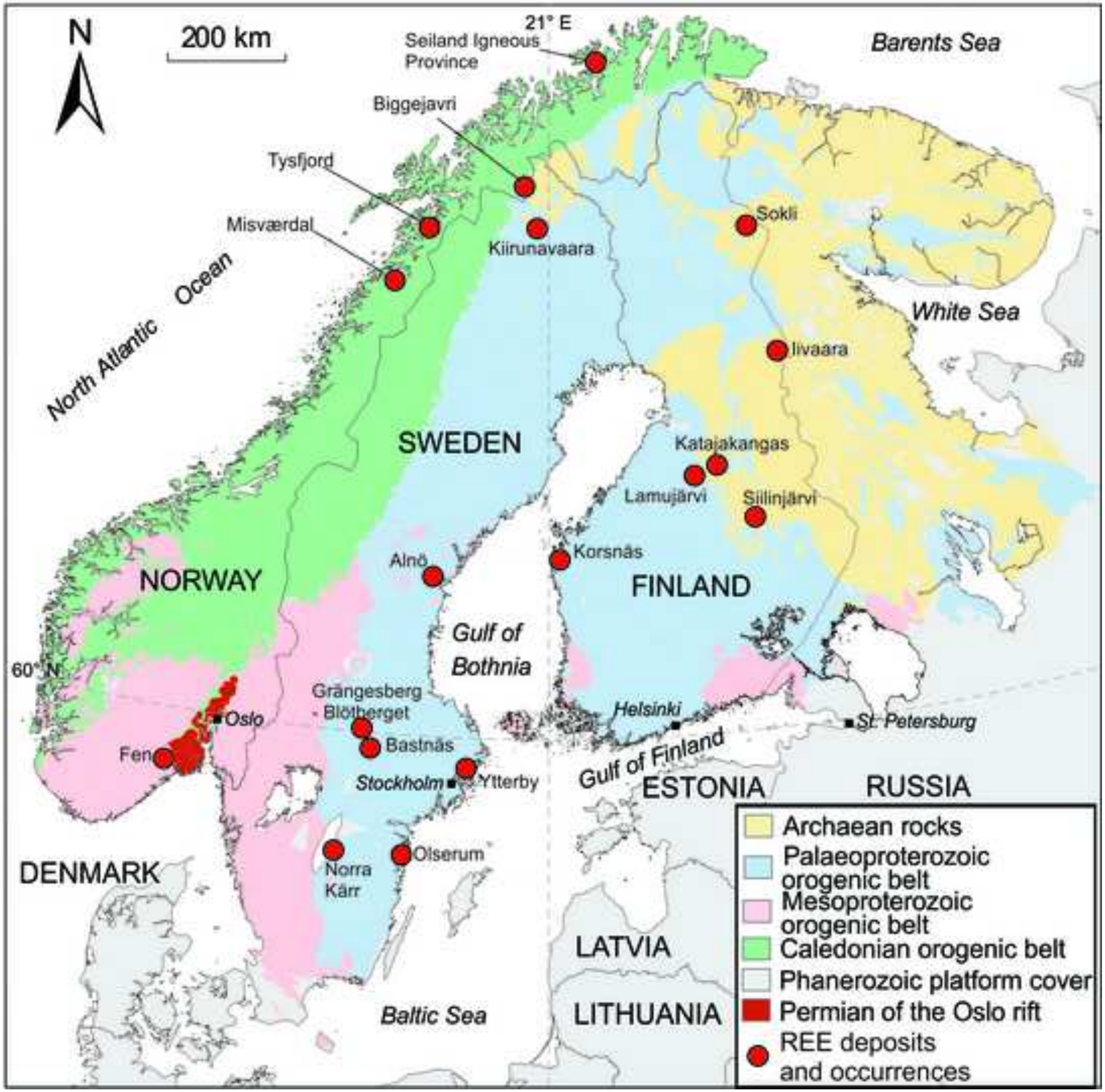

Figure 5

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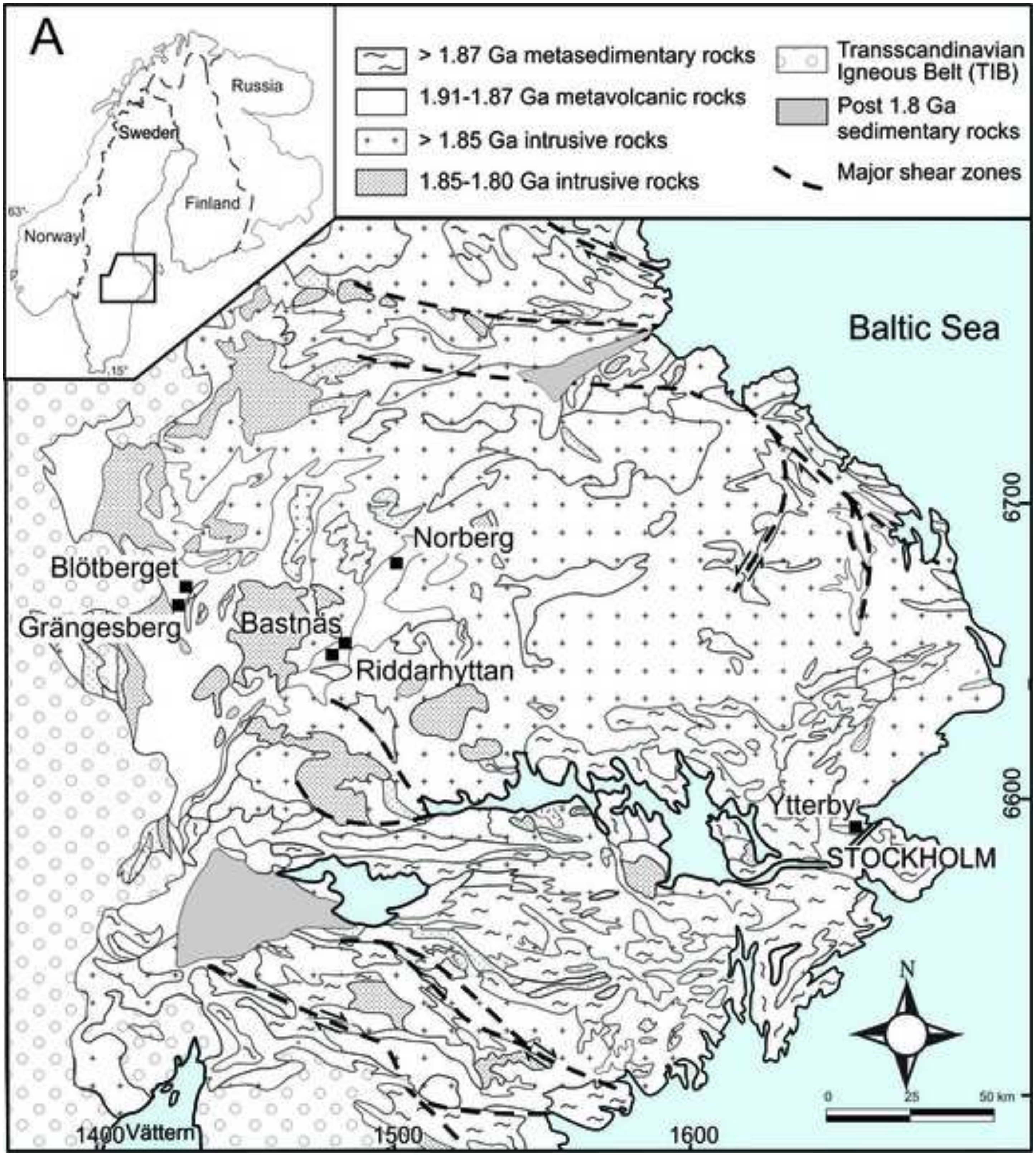


Figure 6

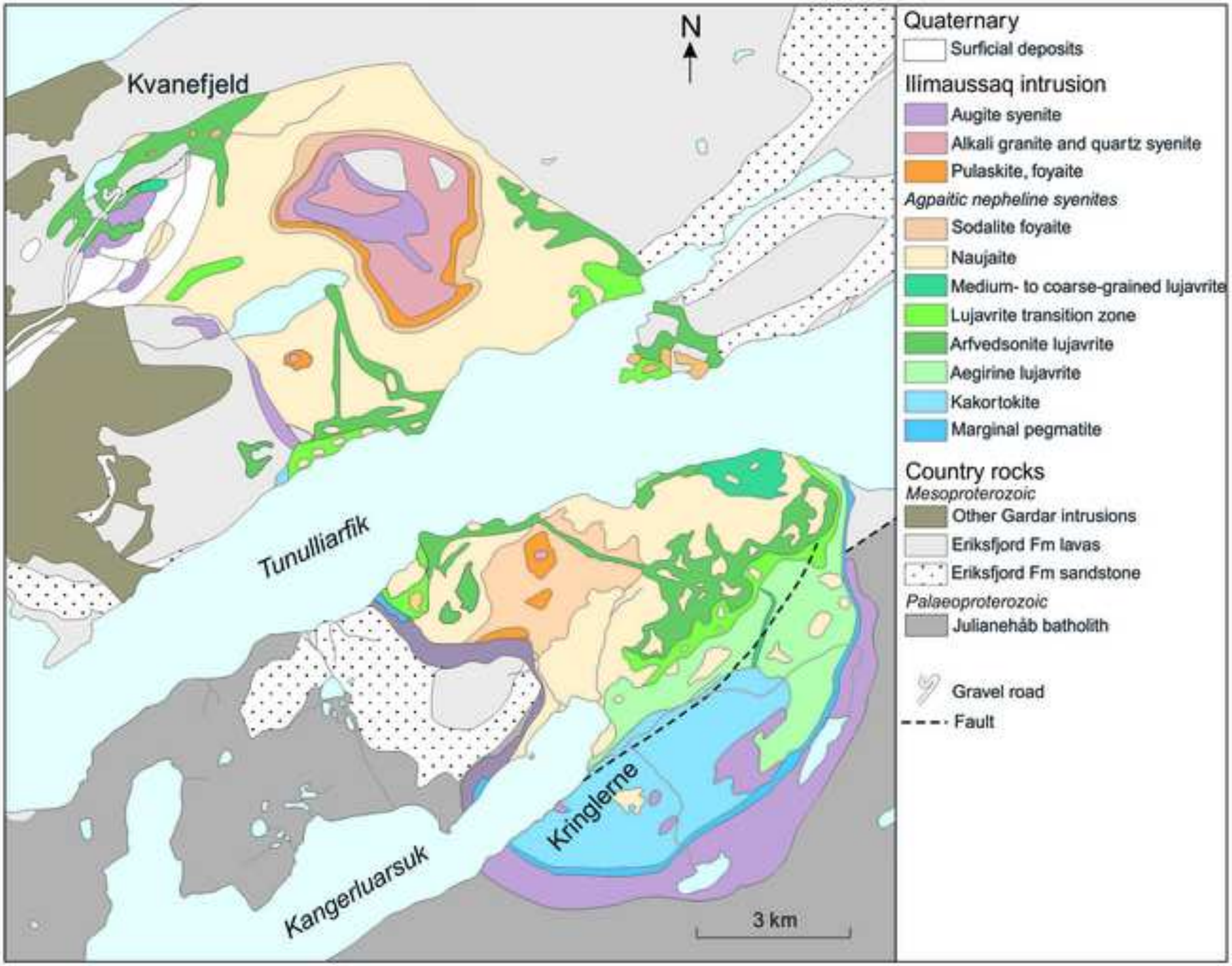
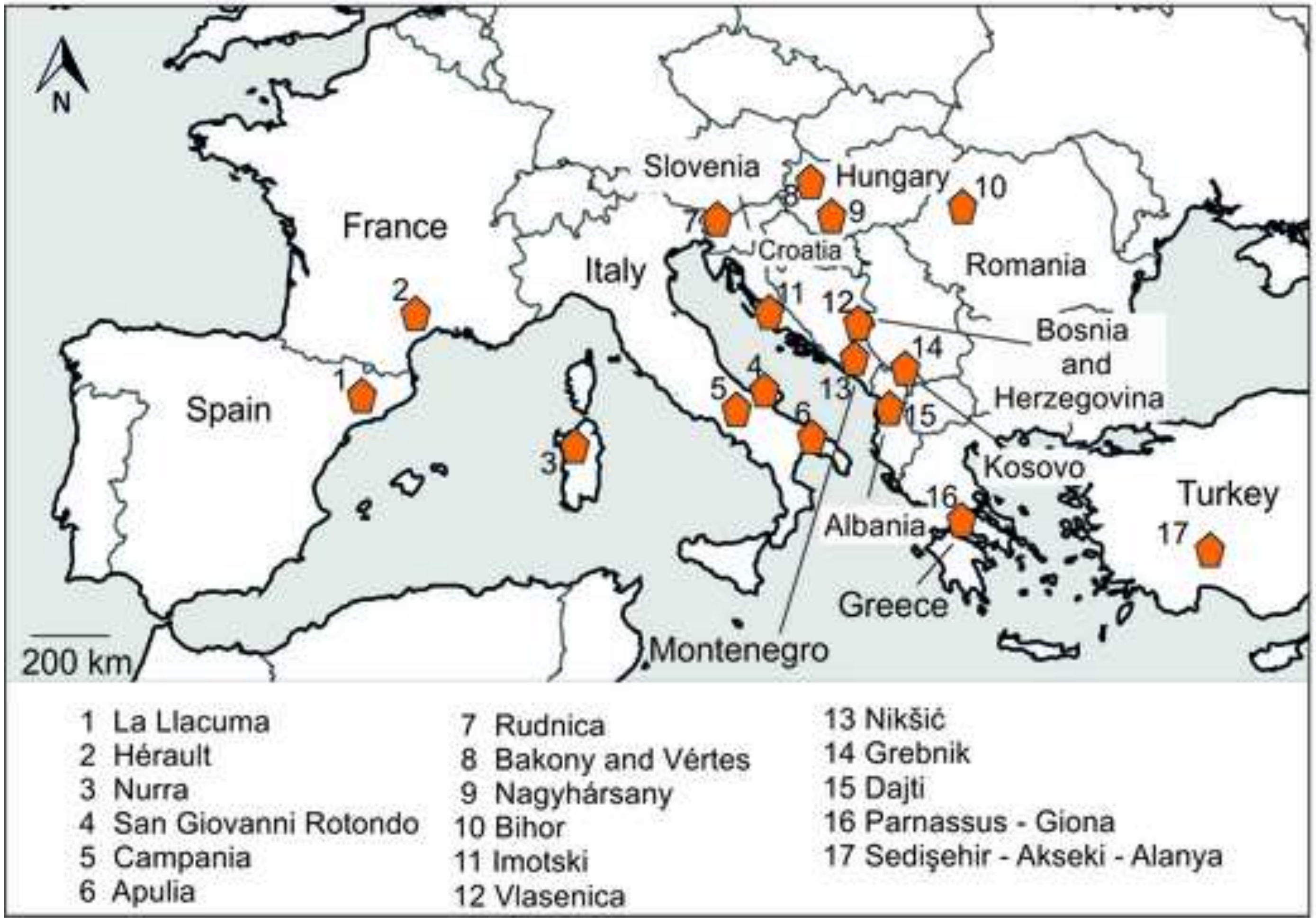

N
Kvanefjeld
Tunulliarfik
Kangerluarsuk
Kringlerne
3 km
Quaternary
Surficial deposits
Ilímaussaq intrusion
Augite syenite
Alkali granite and quartz syenite
Pulaskite, foyaite
Agpaitic nepheline syenites
Sodalite foyaite
Naujaite
Medium- to coarse-grained lujavrite
Lujavrite transition zone
Arfvedsonite lujavrite
Aegirine lujavrite
Kakortokite
Marginal pegmatite
Country rocks
Mesoproterozoic
Other Gardar intrusions
Eriksfjord Fm lavas
Eriksfjord Fm sandstone
Palaeoproterozoic
Julianehåb batholith
Gravel road
Fault

Figure 7


N
200 km
France
Spain
Italy
Slovenia
Croatia
Hungary
Romania
Bosnia and Herzegovina
Kosovo
Albania
Montenegro
Greece
Turkey
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1 La Llacuma
2 Hérault
3 Nurra
4 San Giovanni Rotondo
5 Campania
6 Apulia
7 Rudnica
8 Bakony and Vértes
9 Nagyhársany
10 Bihor
11 Imotski
12 Vlasenica
13 Nikšić
14 Grebnik
15 Dajti
16 Parnassus - Giona
17 Sedişehir - Akseki - Alanya

Table 1

REE-bearing mineral or mineral group*	Formula	Typical deposit types	Examples from this study
Aeschynite*	$\mathrm{REE(Ti,Nb)_2(O,OH)_6}$	Hydrothermal deposits	Galiñeiro, Spain; Ditrãu, Romania
Allanite*	$\mathrm{(REE,Ca)_2(Al,Fe)_3(SiO_4)(Si_2O_7)O(OH)}$	Miaskitic igneous rocks	Loch Loyal, Scotland; Misværdal, Norway; Třebíč, Czech Republic
Ancylite*	$\mathrm{LREE(Sr,Ca)(CO_3)_2(OH).H_2O}$	Carbonatite	Sokli, Finland; Qaqarssuk, Greenland
Apatite*	$\mathrm{Ca_5(PO_4)_3(F,Cl,OH)}$	Carbonatite; Iron oxide–apatite deposits	Siilinjärvi, Finland; Kiruna, Sweden; Sokli, Finland; Kodal, Norway
Bastnäsite*	$\mathrm{REE(CO_3)F}$	Carbonatite; Hydrothermal deposits	Bastnäs, Sweden; Fen, Norway; Sokli, Finland;
Britholite*	$\mathrm{(REE,Ca)_5(SiO_4)_3(OH,F)}$	Hydrothermal deposits	Norberg, Sweden; Korsnäs, Finland
Brockite	$\mathrm{(Ca,Th,Ce)(PO_4).H_2O}$	Hydrothermal deposits	Kizilcaören, Turkey
Burbankite	$\mathrm{(Na,Ca)_3(Sr,Ba,LREE)_3(CO_3)_5}$	Carbonatite	Qaqarssuk, Greenland
Cerite*	$\mathrm{(LREE,Ca)_9(Mg,Ca,Fe^{3+})(SiO_4)_3(SiO_3OH)_4(OH)_3}$	Hydrothermal deposits	Bastnäs, Sweden
Dollaseite*	$\mathrm{CaLREE(Mg_2Al)[Si_2O_7][SiO_4]F(OH)}$	Hydrothermal deposits	Norberg, Sweden
Eudialyte*	$\mathrm{Na_{15}Ca_6Fe_3Zr_3Si(Si_{25}O_{73})(O,OH,H_2O)_3(Cl,OH)_2}$	Agpaitic igneous rocks	Norra Kärr, Sweden; Kringlerne, Greenland
Euxenite*	$\mathrm{(REE,Ca,Th,U)(Nb,Ta,Ti)_2O_6}$	Miaskitic igneous rocks	Třebíč, Czech Republic
Fergusonite*	$\mathrm{REENbO_4}$	Miaskitic igneous rocks	Ditrãu, Romania
Fluocerite*	$\mathrm{REEF_3}$	Hydrothermal deposits	Kizilcaören, Turkey
Gadolinite*	$\mathrm{REE_2Fe^{2+}Be_2O_2(SiO_4)_2}$	Hydrothermal deposits; Miaskitic igneous rocks	Norberg, Sweden; Mourne Mts, N Ireland
Monazite*	$\mathrm{REE(PO_4)}$	Carbonatite; Placers; Hydrothermal deposits; Miaskitic igneous rocks	Olserum, Sweden; Fen, Norway; Central Wales; Ditrãu, Romania
Parisite	$\mathrm{CaLREE_2(CO_3)_3F_2}$	Carbonatite	Fen, Norway
Perrierite*	$\mathrm{REE_4(Mg,\ Fe,Ti)_4O_8(Si_2O_7)_2}$	Placers	Nettuno, Italy
Pyrochlore*	$\mathrm{(Na,Ca)_2Nb_2O_6(OH,F)}$	Carbonatite	Motzfeldt, Greenland; Delitzsch, Germany
Steenstrupine	$\mathrm{Na_{14}REE_6Mn_2Fe^{3+}{}_2Zr(PO_4)_7Si_{12}O_{36}(OH)_2{\cdot}3H_2O}$	Agpaitic igneous rocks	Kvanefjeld, Greenland
Strontianite	$\mathrm{Sr(CO)_3}$	Carbonatite	Siilinjärvi, Finland; Sokli, Finland
Synchysite*	$\mathrm{CaREE(CO_3)_2F}$	Carbonatite; Hydrothermal deposits	Sarfartoq, Greenland
Törnebohmite*	$\mathrm{REE_2Al(SiO_4)_2(OH)}$	Hydrothermal deposits	Bastnäs, Sweden
Västmanlandite	$\mathrm{Ce_3CaMg_2Al_2Si_5O_{19}(OH)_2F}$	Hydrothermal deposits	Norberg, Sweden
Xenotime*	$\mathrm{(Y,HREE)PO_4}$	Hydrothermal deposits; Miaskitic igneous rocks; Placers	Olserum, Sweden; Galiñeiro, Spain; Ditrãu, Romania
Zircon	$\mathrm{ZrSiO_4}$	Miaskitic igneous rocks	Katajakangas, Finland

Annexe 3

Articles scientifiques : Compréhension des processus de minéralisation

Armand, R., Cherubini, C., Tuduri, J., Pastore, N. and Pourret, O., Rare earth elements in French stream waters — Revisiting the geochemical continental cycle using FOREGS dataset. Journal of Geochemical Exploration. DOI: 10.1016/j.gexplo.2015.06.006.

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Rare earth elements in French stream waters — Revisiting the geochemical continental cycle using FOREGS dataset

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A R T I C L E I N F O

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A B S T R A C T

The geochemical behavior of rare earth elements (REEs) has been investigated mainly in geological systems where these elements represent the best proxies of processes involving the occurrence of an interface between different media. This behavior is assessed according to REE concentrations recorded along the REE series normalized with respect to upper continental crust. In this study based on a field approach, the geochemical behavior of REE was investigated in French stream waters. This study is based on FOREGS (Forum of European Geological Surveys) Geochemical dataset that consists on a sampling at regular mesh on all Europe. In France, 119 stream water samples were extracted in drainage basins <100 km^2. The aim of the study is that of describing the spatial variation of REEs and finding the hydro-topo-geochemical factors that affect their distribution by means of a Multivariate Factorial Kriging.

On the basis of their atomic number and of the results of a preliminary Principal Component Analysis three REEs have been selected (La, Eu and Lu) and five physicochemical properties (pH, organic carbon, carbonates, Fe, Mn). A cokriging has been applied that shows a similar spatial organization of REEs: higher values are especially observed in the Aquitaine basin. In order to investigate more deeply on the different sources of variation acting in the study area, a factorial cokriging is applied. The first 2 regionalized factors have been estimated to give a synthetic description of the studied process at the different selected spatial scales. At higher spatial scales (250 km) environmental parameters like Fe, carbonates, and pH, supposed to be ascribed to the rock's nature or to other geological larger scale processes (i.e., hydrographic network and topography), have shown to affect REE distribution. At short range, only Eu and Mn weigh more, which are ascribed to the process of liberation of Mn oxides in rivers that also release the REEs sorbed onto these oxides.

1. Introduction

Rare earth elements (REEs) represent a group of fifteen elements, which share common physiochemical properties and therefore often occur together (McLennan and Taylor, 2012). Over the past 15 years, REEs became of critical importance to many green-technology products and also for medical applications, and therefore are of great economic interest (e.g., Tepe et al., 2014; Guyonnet et al., 2015). In this context as highlighted by Kulaksız and Bau (2013), the continuous development of new technologies and new substances has led to strongly increased release of REEs into natural waters, although their toxicological effects and the potential implications for the ecosystem are often not fully understood. But in aquatic systems, REE concentrations are low compared to their concentrations in rocks with regards to their slight solubility (e.g., Noack et al., 2014). Therefore, it appears important first, to assess and to fully understand the occurrence and fate of aqueous REEs in an environment where REEs release from the anthroposphere may be considered as negligible.

In aquatic systems, solution and interface chemistry appears to be the major factor controlling the REE concentration (e.g., Elderfield et al., 1990; Sholkovitz, 1995). Rare earth elements can form strong complexes with a number of different ligands. For convenience, REE concentrations of continental waters are usually normalized to Upper Continental Crust (UCC; McLennan, 2001), which produces smooth REE_{UCC} distribution patterns. The REE patterns result from the combination of several processes able to induce their fractionation. These processes are themselves controlled by several physicochemical mechanisms and parameters. Three processes can be distinguished: (i) precipitation/dissolution, (ii) sorption onto colloids and particles, and (iii) complexation in solution with organic and inorganic ligands. The resulting REE pattern therefore corresponds to the REE pattern for mineral sources that are modified by the sorption/complexation with ligands, colloids and particles. This results in a wide range of diverse REE patterns, which can be characterized by a depletion or enrichment

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degree of light REEs (LREEs) relative to heavy REEs (HREEs) or by whether or not anomalies occur. Indeed, individual REEs may show anomalous behavior in natural waters: redox-sensitive Ce and Eu may show anomalies that may be used as redox- and/or temperature-proxies (e.g., Bau, 1991; De Baar et al., 1988), and La, Gd and Lu may show small anomalies due to subtle differences between the stabilities of REE complexes (Bau, 1999; Byrne and Kim, 1990). In addition to these natural anomalies, anthropogenic anomalies of Gd and, recently, La and Sm have been reported from natural waters (e.g., Kulaksız and Bau, 2013, and references therein).

To better understand the occurrence of aqueous metals and especially REEs, the FOREGS (Forum of European Geological Surveys) aims at providing a basis for formulating policies and legislation concerning the management of harmful elements and to define their corresponding safety levels (Salminen et al., 2005). A first attempt was performed in Italy, Sweden and Europe by Imrie et al. (2008), Lado et al. (2008), Petrosino et al. (2013), and Sadeghi et al. (2013). These studies mostly focus on topsoil dataset and investigate the main factors explaining REE variation in the soil solution; however, the FOREGS database contains descriptions of other environmental media (stream and floodplain sediments, and stream water). The database has been processed by Imrie et al. (2008), Lado et al. (2008), Petrosino et al. (2013) and Sadeghi et al. (2013) by means of multivariate approaches to interpolate all variables, metals or REE concentrations. They used factorial kriging for Imrie et al. (2008), regression kriging for Lado et al. (2008) and inverse distance weighted interpolation and principal component analysis for Sadeghi et al. (2013). The results associate spatial distribution of elements with different factors operating at several scales. For example, Imrie et al. (2008) highlight four factors and among them (i) a short scale (72 km): concentrations may be explained by parent material geology, land use and organic matter content; and (ii) a medium scale (296 km): concentrations may be explained by major structural division of European continent and the distribution of calcareous rocks. Petrosino et al. (2013) show that in Italy and Sweden, REE concentration in all sampling medias are related to the geological context. In the particular case of stream water, they found that Swedish waters are more concentrated in REEs than Italian waters. These authors relate high REE concentrations to water acidity (linked to vegetation and felsic rocks). Whereas, in Italy, pH is higher and the watershed is mostly composed of calcareous rocks which mostly explain the lower REE contents as already highlighted by Johannesson and Burdige (2007) or Deberdt et al. (2002).

As the chemistry of stream waters is influenced by several landscape factors which are related to geology, topography, climate, and vegetation (e.g., Andersson and Nyberg, 2009; Gaillardet et al., 2014); the aim of this study is to further investigate the FOREGS dataset focusing on France. A special attention will be given to REE pattern spatial distribution. For such needs, the FOREGS stream dataset was processed by means of geostatistical methods, especially by factor kriging analysis. These approaches have three steps described as follows: (i) modeling the coregionalization of the set of variables, (ii) analyzing the correlation structure between the variables by applying principal component analysis, and (iii) cokriging specific factors at each characteristic scale. The 14 REE concentrations available in the dataset were all used as inputs, as well as some physicochemical properties: pH, carbonate alkalinity, Fe, Mn and organic carbon. The obtained maps allow visualizing the factors which integrate REE spatial variability. This variability is discussed with some landscape factors, especially topography and upstream/downstream location.

2. Materials and methods

2.1. The study area

The geology of France results of a succession of events related to assembly and disruption of Gondwana and Pangea megacontinents and climate changes. Geographically, France has acquired a rugged topography giving it a wide range of outcropping terranes spanning from Proterozoic to Cenozoic (Fig. 1). France can be divided into four geological terranes. (i) France is mostly covered by Mesozoic and Cenozoic deposits which correspond to intracratonic sedimentary basins like Paris Basin or Aquitaine Basin (Biteau et al., 2006; Guillocheau et al., 2000). These extensive areas have been scarcely deformed and are characterized by small dip values and concentric rock deposits. The tabular structure involves typical landscapes like alluvial plains, plateau and hills. In addition to intracratonic genesis, other basins correspond to grabens formed during Alps orogeny (Rhein and Limagnes graben). These units are generally depressions filled with Cenozoic sediments. (ii) These Mesozoic and Cenozoic sedimentary units lay on a basement composed of Paleozoic and Proterozoic rocks (Ballèvre et al., 2009; Faure et al., 2009). The basement is widely metamorphic and magmatic and is surrounded by discordant Mesozoic sedimentary cover. It constitutes the essential part of eroded mountain ranges like Vosges, Armorican Massif or French Massif Central erected during Cadomian and Variscan orogeny (Ballèvre et al., 2009; Faure et al., 2009). These reliefs have been strongly flattened by erosion, except to Vosges and French Massif Central which have been uplifted again during Alps orogeny (Faure et al., 2009). (iii) Alps and Pyrenees are recent mountain ranges still erecting since Upper Cretaceous (Choukroune, 1992; Lagabrielle and Lemoine, 1997; Rosenbaum and Lister, 2005; Vissers and Meijer, 2012). These ranges form a complex association between Meso-Cenozoic rocks which have been heavily deformed due to fault and folding action and basement units. The resulting landscape is high mountains (Valla et al., 2011). (iv) Recent volcanic ranges are located massively in the Massif Central (Michon and Merle, 2001). These units are mainly composed of basalts, trachytes, and rhyolites, aged from Neogene (Cantal) to Pleistocene (Chaîne des Puys).

2.2. The FOREGS dataset

The FOREGS program uses standardized field, analytical and quality control procedures to produce reliable reproducible geochemical data over Europe (Salminen et al., 1998). Therefore, the FOREGS initiated a program to construct a geochemical database with the aim of compiling the first geochemical atlas of Europe (Fedele et al., 2008). The field manual by Salminen et al. (1998) is the basis for a decade-long project, involving geochemists from 26 countries, which led to the publication of the Geochemical Atlas of Europe (De Vos and Tarvainen, 2006; Salminen et al., 2005). As a result, a large geochemical database is now available free for public use[1] (De Vos and Tarvainen, 2006; Salminen et al., 2005).

2.2.1. Sampling strategy

The FOREGS sampling grid (Salminen et al., 1998; Tarvainen et al., 2005) was based on the Global Terrestrial Network (GTN) grid composed of 160 × 160 km cells and developed for the purpose of Global Geochemical Baselines Mapping (Darnley et al., 1995). For each cell, five randomly generated sites were selected, according to the following scheme:

- Point number 1 is located in the NE quadrant of the GTN grid cell;
- Point number 2 in the NW quadrant;
- Point number 3 in the SW quadrant;
- Point number 4 in the SE quadrant; and
- Point number 5 is randomly located in anyone of the four quadrants of the GTN grid cell.

As a result, France was divided into 25 cells and 119 sample sites were determined. Based on former randomly generated points, five nearest small drainage basins of <100 km^2 were selected. For each

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[1] http://weppi.gtk.fi/publ/foregsatlas/index.php.

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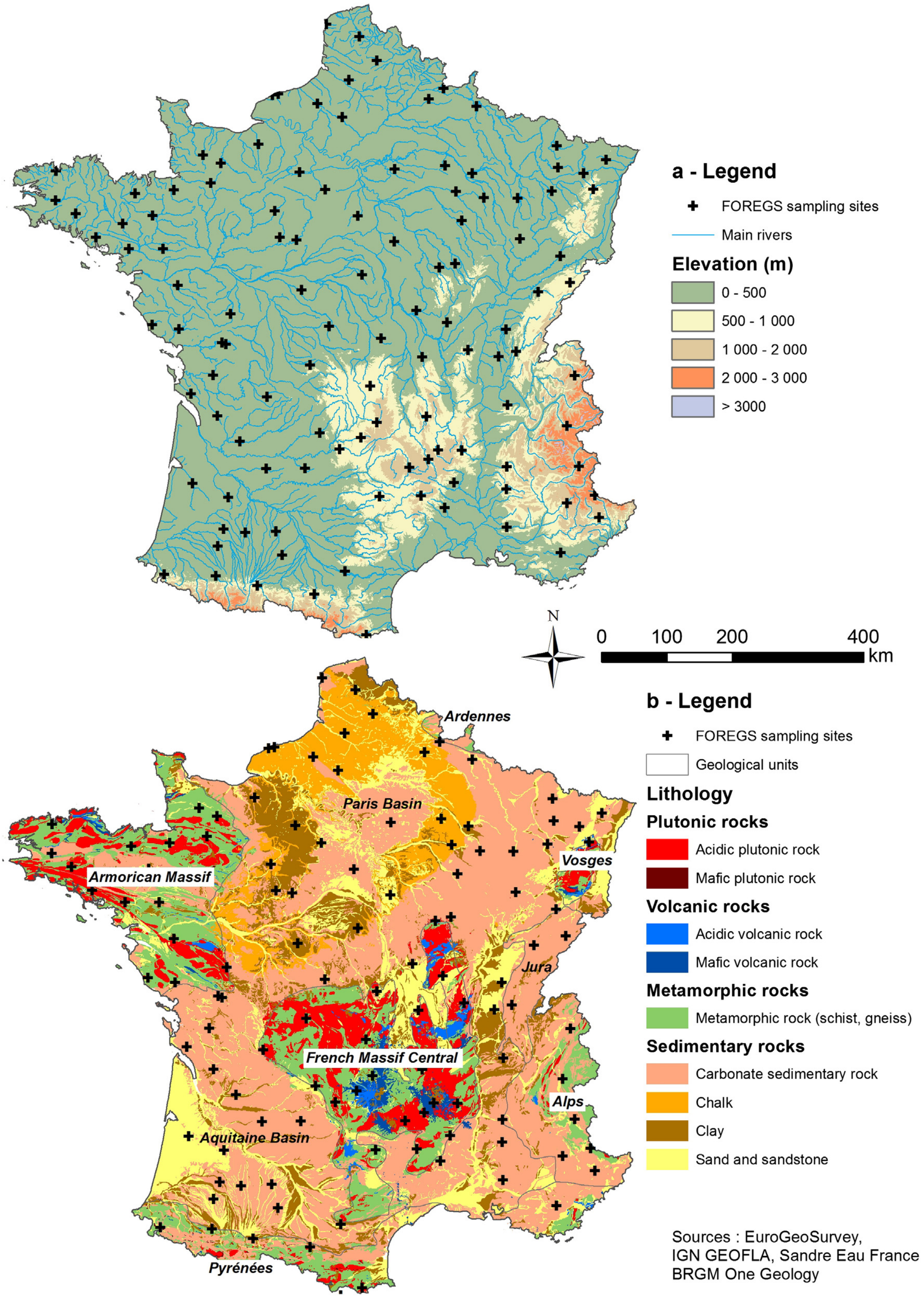

Sources : EuroGeoSurvey,
IGN GEOFLA, Sandre Eau France
BRGM One Geology

Fig. 1. Simplified maps of (a) elevation and (b) geological units.

cell, a larger drainage basin (area 1000–6000 km^2), to which the small drainage basin is connected, was selected. The floodplain sediment samples were collected either from a suitable point near its outlet with the sea or the confluence point with another major river system. In this study, French stream water samples were selected. The dataset consists of 119 sampling sites (one sample per site). However, 4 sites located in Corsica were removed of the dataset to obtain a homogeneous spatial distribution. Samples were collected during two periods of the winter: from November 1998 to December 1998; and from March 1999 to October 1999. Sampling during rainy periods and flood

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events was avoided. According to FOREGS stream water sampling procedure, running stream water was collected from the small, second order, drainage basins (<100 km^2). Physico-chemical parameters (pH, temperature and electrical conductivity) were measured at the site while several stream water samples were collected. ICP–MS analyses were performed on a 100 mL sample filtered to 0.45 μm (Salminen et al., 1998).

2.2.2. Chemical analyses and quality controls

As described in Sandström et al. (2005): stream water samples were acidified to 1% v/v with nitric acid and stored at less than 8 °C. The samples were analyzed by both inductively coupled plasma quadrupole mass spectrometry (ICP–QMS) and inductively coupled plasma atomic emission spectrometry (ICP–AES), using Perkin Elmer Sciex ELAN 5000A and Spectro Flame M instruments respectively, in accordance with the German norms DIN 38406-29 (ICP–MS) and DIN 38406-22 (ICP–AES). Analyses were performed by BGR (Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany). The primary chemicals used to prepare the calibration and quality control standards and reagents were of analytical reagent grade. Multi-element standard solutions for calibration were prepared from Claritas SPEX/Certiprep stock solutions. International certified reference materials (NIST 1640, NIST 1643d and SLSR-4) were included in every batch of 20 samples. Indium was used as an internal standard. The accuracy of the methods for all determinants is better than ±10%, the bias is within ±3%, and the repeatability at the 95% confidence interval is better than 5% at concentrations an order of magnitude above the limit of quantification. Limits of quantification for all cations and trace metals are given in Sandström et al. (2005).

2.3. Geographic information system and multivariate geostatistical approach

Geographic information system (GIS) analysis was performed with ArcGis 10 software. Distance between sample site and outlet was calculated using the BD Carthage (Sandre Eau France) dataset which is the French official dataset about hydrographic network. Geological context of sampling sites was obtained by GIS intersection with 1/1,000,000 geological units (BRGM One Geology).

Concentrations of 14 REEs and physicochemical properties (pH, carbonate alkalinity as HCO_3, Fe, Mn and organic carbon) were used as inputs for the geostatistical method. Descriptive statistics (mean, standard deviation sd, median med, and median absolute deviation MAD) were performed on all variables and normality of data and homogeneity of variances were verified. As data behave following a not normal distribution, non-parametric Kruskal–Wallis tests were performed to quantify differences in variables within geological contexts.

The multivariate spatial data were analyzed by cokriging and Factor Kriging Analysis (FKA) which is a geostatistical method developed by Matheron (1982). The FKA consists of decomposing the set of original second-order random stationary variables $\{Z_i(x), i = 1,\ldots, n;\}$ into a set of reciprocally orthogonal regionalized factors $\{Y^u_v(x), \nu = 1,\ldots, n; u = 1,\ldots, N_s\}$ where N_S is the number of spatial scales, through transformation coefficients a^u_{iv} (loadings components score) combining the spatial with the multivariate decomposition:

$$Z_i(x) = \sum_{u=1}^{N_S} \sum_{v=1}^{n} a^u_{iv} Y^u_v(x).$$

The three basic steps of FKA are the following:

(i) Modeling the coregionalization of the set of variables, using the so called Linear Model of Coregionalization (LMC);
(ii) Analyzing the correlation structure between the variables, by applying Principal Component Analysis (PCA) at each spatial scale; and
(iii) Cokriging specific factors at each characteristic scale and mapping them.

2.3.1. Linear model of coregionalization

The LMC, developed by Journel and Huijbregts (1978), considers all the studied variables as the result of the same independent physical processes, acting at different spatial scales u. The $n(n+1)/2$ simple and cross variograms of the p variables are modeled by a linear combination of N_S standardized variograms to unit sill $g^u(h)$. Using the matrix notation, the LMC can be written as:

$$\Gamma(h) = \sum_{u=1}^{N_S} B^u g^u(h)$$

where $\Gamma(h) = [\gamma_{ij}(h)]$ is a symmetric matrix of order $n \times n$, whose diagonal and non-diagonal elements represent simple and cross variograms for lag h; $B^u = [b^u_{ij}]$ is called coregionalization matrix and it is a symmetric semi-definite matrix of order $n \times n$ with real elements b^u_{ij} at a specific spatial scale u. The model is authorized if the functions $g^u(h)$ are authorized variogram models. In the LMC the spatial behavior of the variables is supposed resulting from superimposition of different independent processes working at different spatial scales. These processes may affect the behavior of experimental semi-variograms, which can then be modeled by a set of functions $g^u(h)$. The choice of number and characteristics (model, sill, range) of the functions $g^u(h)$ is quite delicate and can be made easier by a good experience of the studied phenomena (Chilès and Guillen, 1984). Fitting of LMC is performed by weighed least-squares approximation under the constraint of positive semi-definiteness of the B^u, using the iterative procedures developed by Goulard (1989). The best model was chosen, as suggested by Goulard and Voltz (1992), by comparing the goodness of fit for several combinations of functions of $g^u(h)$ with different ranges in terms of the weighted sum of squares.

2.3.2. Regionalized principal component analysis

Regionalized Principal Component Analysis consists of decomposing each coregionalization matrix $\boldsymbol{B}^u$ into two other diagonal matrices: the matrix of eigenvectors and the diagonal matrix of eigenvalues for each spatial scale u through the matrix $\boldsymbol{A}^u$ of order $n \times n$ of the transformation coefficients a^u_{iv} (Wackernagel, 2003). The transformation coefficients a^u_{iv} in the matrix $\boldsymbol{A}^u$ correspond to the covariances between the original variables $Z_i(x)$ and the regionalized factors $Y^u_v(x)$.

2.3.3. Mapping multivariate spatial information

The behavior and relationships among variables at different spatial scales can be displayed by interpolating the regionalized factors $Y^u_v(x)$ using cokriging and mapping them (Castrignanò et al., 2000, 2007). The cokriging system in FKA has been widely described by Wackernagel (2003).

3. Results

3.1. Relationships between stream data and geology

Table 1 shows the descriptive statistics of all variables between the geological contexts. The majority of the 115 samples is located in sedimentary areas (n = 85), among them 40 are carbonate derived rocks, 9 chalks, 12 clays and 24 sand and sandstones. The others are located in metamorphic (n = 18), acidic plutonic (n = 8) and acidic volcanic (n = 3) contexts. Most of physicochemical properties and selected REEs show significant differences between the geological contexts: pH, carbonate alkalinity, Fe, La and Lu. This suggests the influence of surrounding rocks geology on water chemistry. Water samples taken from sedimentary areas are characterized by higher carbonate alkalinity concentrations (from 69 mg/L to 134 mg/L) and alkaline pH value (from 7.68 to 8.02) which is explained by carbonates presence in sedimentary rocks. Higher Fe concentrations (176 mg/L and 224 mg/L respectively) are observed in both acidic plutonic and metamorphic areas. Regarding

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Table 1
Descriptive statistics of selected REEs and physicochemical properties.

Geological context		pH				HCO_3 (mg/L)				OC (mg/L)				Fe (μg/L)				Mn (μg/L)			
	n	Mean	sd	Med	MAD	Mean	sd	Med	MAD	Mean	sd	Med	MAD	Mean	sd	Med	MAD	Mean	sd	Med	MAD
Acidic plutonic rock	8	6.99	0.42	7.00	0.20	30.12	31.74	18.17	5.24	5.02	3.28	4.05	1.80	176.48	114.55	150.00	81.05	16.24	10.69	13.75	6.95
Acidic volcanic rock	3	7.03	0.85	6.70	0.30	31.14	8.61	34.00	3.95	1.82	0.77	1.85	0.73	74.90	30.96	83.00	18.00	11.42	6.07	10.20	4.15
Metamorphic rock (schist. gneiss…)	18	7.42	0.67	7.20	0.30	50.80	47.08	34.63	12.50	5.03	3.79	4.57	2.70	224.47	161.12	229.00	154.78	23.73	23.55	15.50	10.45
Carbonate sedimentary rock	40	8.02	0.67	8.10	0.10	230.87	114.18	277.98	65.84	2.89	3.70	1.97	0.90	46.78	68.82	18.23	9.60	17.45	28.19	3.61	3.24
Chalk	9	7.79	0.67	7.75	0.10	276.11	69.14	300.23	24.08	4.50	3.44	3.41	1.71	65.33	93.12	32.60	24.02	14.16	10.19	11.30	7.10
Clay	12	7.68	0.67	7.80	0.25	163.49	133.96	113.15	91.75	3.61	2.25	3.68	1.74	108.56	126.34	60.77	45.12	34.11	44.31	20.55	13.90
Sand and sandstone	24	7.80	0.67	8.00	0.20	174.60	130.85	131.67	106.31	4.35	2.96	3.80	1.95	137.25	211.21	37.40	28.39	25.73	28.36	15.71	11.18
No data	1																				
Kruskal–Wallis p-value		***				***				*				***				NS			

Geological context		La (μg/L)				Eu (μg/L)				Lu (μg/L)			
	n	Mean	sd	Med	MAD	Mean	sd	Med	MAD	Mean	sd	Med	MAD
Acidic plutonic rock	8	0.1491	0.0905	0.1490	0.0680	0.0083	0.0036	0.0070	0.0020	0.0031	0.0014	0.0030	0.0010
Acidic volcanic rock	3	0.0717	0.0071	0.0730	0.0050	0.0040	0.0010	0.0040	0.0010	0.0013	0.0006	0.0010	<0.001
Metamorphic rock (schist. gneiss…)	18	0.1374	0.1076	0.1250	0.0930	0.0095	0.0057	0.0080	0.0040	0.0031	0.0019	0.0030	0.0020
Carbonate sedimentary rock	40	0.0280	0.0441	0.0170	0.0130	0.0055	0.0043	0.0050	0.0030	0.0013	0.0009	0.0010	<0.001
Chalk	9	0.0720	0.1333	0.0190	0.0090	0.0049	0.0069	0.0020	0.0010	0.0018	0.0016	0.0010	<0.001
Clay	12	0.0850	0.1267	0.0380	0.0240	0.0080	0.0087	0.0050	0.0030	0.0020	0.0018	0.0010	<0.001
Sand and sandstone	24	0.0941	0.1278	0.0340	0.0260	0.0080	0.0078	0.0050	0.0030	0.0025	0.0026	0.0010	<0.001
No data	1												
Kruskal–Wallis p-value		***				*				***			

NS = non-significant.
*** $p < 0.001$.
* $p < 0.05$.

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Table 2
Principal component analysis: obtained components.

Component	Eigenvalue	Variance (%)	Cumulative variance
F1	22.66	84.5	84.5
F2	1.62	6.1	90.6

La, Eu and Lu concentrations, higher concentrations are observed in samples taken from metamorphic and plutonic areas (0.1491 μg/L and 0.1374 μg/L for La, respectively) whereas lower concentrations are derived from carbonate rocks (0.0280 μg/L for La). This is consistent with REE sources essentially located in metamorphic and magmatic rocks (from 50 to 100 mg/kg for La; Henderson, 1984; McLennan, 1989) whereas REE content in carbonates is low (10 mg/kg for La; Turekian and Wedepohl, 1961).

3.2. Principal component analysis

The classical statistical technique based on the PCA has been applied in order to investigate on the behavior of the variables in relation to the principal components. Since geochemical data are compositional, every data set should be opened, prior to its statistical treatment, using a preferred method from a variety of suggested methods (Sadeghi et al., 2014). In this study, statistical PCA has been performed using the ln-transformed data sets (Pawlowsky-Glahn and Buccianti, 2011). The generated results are given in Table 2. The PCA, performed in this study, using ln-transformed data has successfully opened the data. Using PCA, two principal components were extracted that cumulatively explained 90.6% of the total data variability and with an eigenvalue greater than 1 (Table 2). The other components had an eigenvalue less than 1 and were not used. Generally, the first components account for most of the variability contained in the data set (Johnson and Wichern, 2002). In the case study the first two principal components were used in the analysis, mainly due to the presence of such correlations with the real properties, as shown in the circle of correlations presented in Fig. 2. The circle of correlation shows the proximity of the variables inside a unit circle and is useful to evaluate the affinity and the antagonism between the variables. Statement can easily be made about variables which are located near the circumference of the unit circle. In our case the first component is highly correlated with all REEs and also Fe, while the Mn, OC, pH, and carbonate alkalinity are located a little further away from the circumference and appear to have a different behavior. They all are correlated negatively with the F2. From an analysis of the circle it is possible to see that all the HREEs are positioned in the upper part and all the LREEs in the lower part of the semi circumference. Europium shows a slightly different behavior as it is more detached from the circumference, and is close to Fe. From the PCA it appears that the first regionalized factor explains the behavior of the REEs and separates them from the other elements. No substantial additional information is provided by the F2.

3.3. Coregionalization analysis

The variables are highly shifted from the Gaussian distribution so they were normalized and standardized to mean 0 and variance 1. On the basis of the results of principal component analysis, a choice has been made between the 19 variables. The chosen parameters are Fe, Mn, carbonate alkalinity, organic carbon and pH for the physicochemical properties together with La, Lu and Eu for the REEs. La is representative of LREEs, Lu of HREEs and Eu has been chosen because of his peculiar behavior (McLennan and Taylor, 2012). Using GAMV of GSLIB library (Deutsch and Journel, 1992) the experimental variograms and cross-variograms of the 3 REEs and Fe, Mn, carbonate alkalinity, organic carbon and pH have been obtained with lag separation distance equal to 20 km. No relevant anisotropy was observed in the variogram maps and the experimental variograms looked upper bounded. The linear coregionalization model has been obtained using the LCMFIT2 program (Pardo-Iguzquiza and Dowd, 2002) to fit the 36 experimental variograms. The LMC was fitted using two spatial structures: a spherical model with a range of 120 km and a spherical model with a range of 250 km. The linear coregionalization models (direct and cross-variograms) (not shown) appear well spatially structured also due to the absence of the not-spatially correlated component (nugget effect). The spatial cross-correlation is shown in Table 3. The appropriateness of the LCM and the basic structures was evaluated with a cross-validation test by calculating the mean error and the variance of standardized error, which were quite close to 0 (varying between −0.033 and 0.0145) and 1 (varying between 0.9 and 1.2), respectively. These results mean that the estimates were unbiased and the estimation variance reproduced the experimental variance accurately.

3.4. Factorial kriging

Using FACTOR2d program (Pardo-Iguzquiza and Dowd, 2002) a factorial cokriging is used to estimate the first 2 regionalized individual factors that, at the cost of an acceptable loss of information, have given a synthetic description of the process in study at the different selected

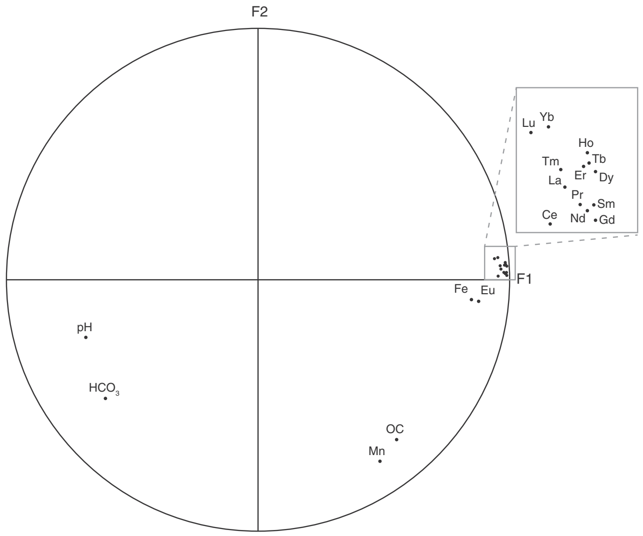

Fig. 2. Principal component analysis: circle of correlations.

Table 3
Structural correlation coefficients.

	Eu	Fe	HCO_3	La	Lu	Mn	OC	pH
Short range h = 120 km								
Eu	1.000							
Fe	0.640	1.000						
HCO_3	−0.174	−0.227	1.000					
La	0.772	0.525	−0.474	1.000				
Lu	0.682	0.444	−0.409	0.568	1.000			
Mn	0.644	0.856	−0.156	0.533	0.315	1.000		
OC	0.735	0.409	0.000	0.251	0.364	0.400	1.000	
pH	−0.261	−0.181	0.403	−0.191	−0.331	−0.191	0.000	1.000
Long range h = 250 km								
Eu	1.000							
Fe	0.879	1.000						
HCO_3	−0.987	−0.845	1.000					
La	0.734	0.958	−0.718	1.000				
Lu	0.865	0.995	−0.823	0.957	1.000			
Mn	0.109	0.561	−0.087	0.752	0.572	1.000		
OC	0.428	0.796	−0.355	0.858	0.802	0.873	1.000	
pH	−0.739	−0.922	0.750	−0.981	−0.920	−0.705	−0.752	1.000

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Table 4
Correlation between factors and original variables.

	Factor 1	Factor 2
Short range h = 120 km		
Eu	0.773	0.146
Fe	0.493	0.106
HCO_3	−0.256	0.437
La	0.441	−0.044
Lu	0.519	−0.148
Mn	0.687	0.183
OC	0.378	0.252
pH	−0.296	0.580
Explained variance (%)	50.0	20.2
Long range h = 250 km		
Eu	−0.436	0.294
Fe	0.796	−0.074
HCO_3	−0.607	0.452
La	0.814	0.104
Lu	0.603	−0.042
Mn	0.374	0.423
OC	0.639	0.393
pH	−0.648	−0.029
Explained variance (%)	80.3	17.0

spatial scales. As no nugget effect has been modeled, the short-range and long-range components of the first two regionalized factors were selected. The long range component (250 km) of the first two factors explains most variance (80.3% and 17.0%, respectively) while the short range component explains just the 50.0% and 20.2% for F1 and F2 respectively, which is less representative. The long range component of the first factor shows to be the most explicative as it is correlated with most of the elements positively, such as Fe (0.796), La (0.814), Lu (0.603), organic carbon (0.639) and negatively with HCO_3^- (−0.607), and pH (−0.648) (Table 4). The F1 at long range synthesizes the long range variability of the whole elements with a localized higher value zone in the central and south-eastern part. The short range component (120 km) of the first factor is mostly correlated with Eu (0.773) and Mn (0.687). Europium shows a different behavior being mostly explained by the F1 at the short spatial scale. However, in order to get more precise information about its structure, additional data should be collected to infer the variability at a smaller spatial scale. As far as the F2, it does not show to be correlated at all with the REEs but it is correlated more with the physico-chemical parameters, such as with the pH at small spatial scale (0.580).

3.5. Cokriging

Cokriging was applied to the transformed data to obtain the estimates which were then back-transformed to express them in the original variables. The spatial maps of the eleven variables were obtained by cokriging on a 10 km × 10 km square grid. Figs. 3, 4 and 5 represent, respectively, the first regionalized factor at short range and at long range, the 3 selected REEs and the 5 physicochemical properties. From an analysis of the cokriged maps it is possible to see that REEs exhibit all similar spatial distributions, with extended higher values in the south-western part, in correspondence with the depression of Aquitaine basin (low area surrounded by higher land and usually characterized by interior drainage). Other zones of localized higher value correspond with the Alpine valley corridors of the Rhône, the hydrographic network of the Seine basin, hydrographic network of the Loire with its effluents. Another zone of higher values is localized in correspondence of the Oise basin, in the Paris basin. The anisotropy (SW–NE for the southern part and NW–SE for the northern part of France) showed in the maps of REEs is coherent with the direction of propagation of rivers except for the Aquitaine basin where the high concentrations are due to the interior drainage of the low area. Organic carbon and Mn show similar behavior having higher zone values concentrated in the same areas of the REEs, while carbonate alkalinity and pH, show a totally contrasting behavior with the rest of the variables (being negatively correlated).

4. Discussion

4.1. Assessment of factor kriging analysis

The long range component of the first factor shows to be the most explicative (80.3% of the variance) as it synthesizes the long range variability of most of the elements (Fe, La, Lu, organic carbon, carbonate alkalinity and pH) with a localized higher value zone in the central and south-eastern part. Therefore at high spatial scales environmental parameters like Fe, carbonates, pH, are supposed be ascribed to the rock's nature or to other larger scale processes (i.e., river network). The structure of the hydrographic network is determined by a complex of physicogeographic conditions especially by climate, by the topography, and by the geological structure of the locality. Indeed, hydrographic network and topography have shown to affect REE distribution (e.g., Köhler et al., 2014). The short range component of the first factor explains just the 50.0% of the variance and is mostly correlated with Eu (0.773) and Mn (0.687). So at short range, just the Eu and Mn weigh more, which are ascribed to the process of Mn oxides release in rivers

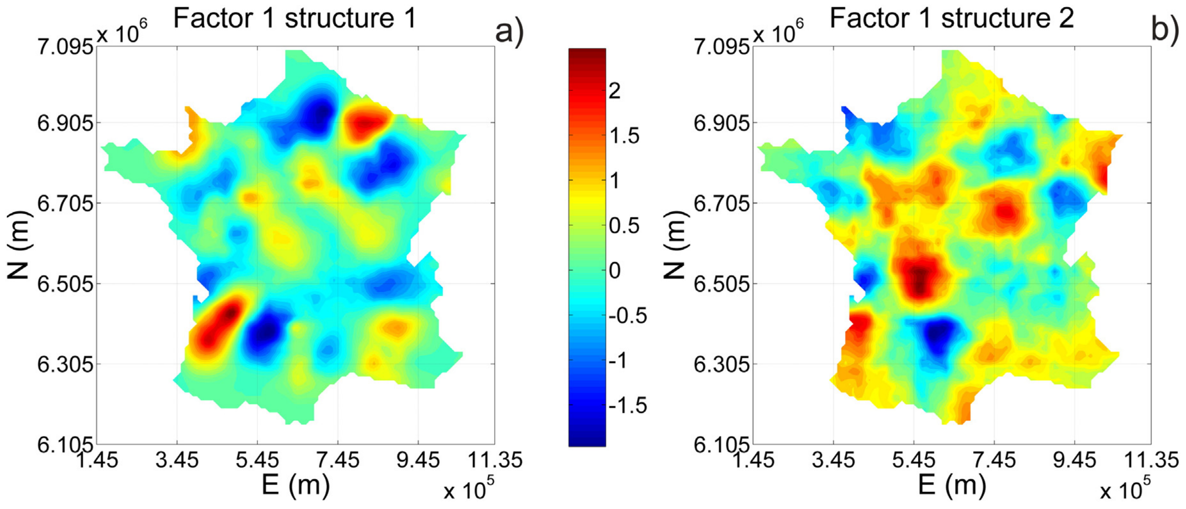

Fig. 3. First regionalized factor at short (structure 1) and at long range (structure 2).

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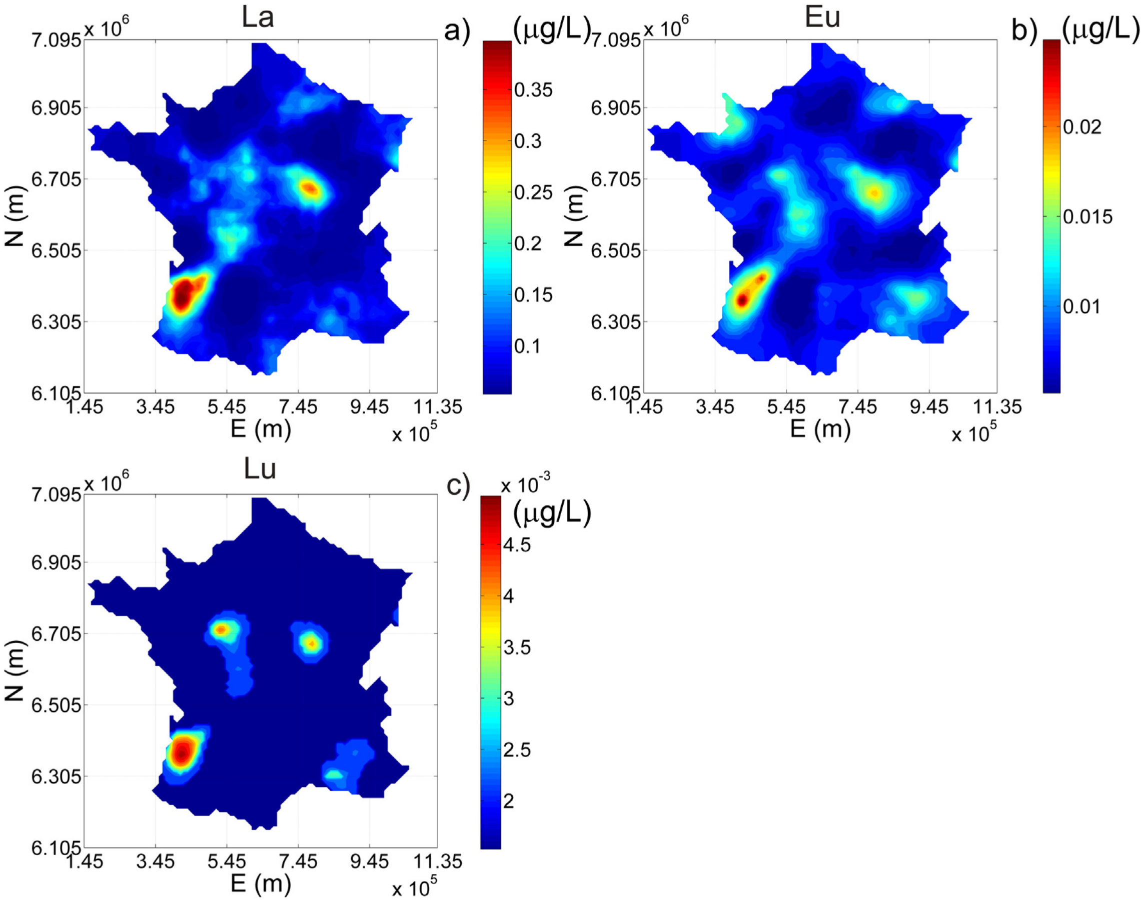

Fig. 4. Cokrigged maps of (a) La, (b) Eu, and (c) Lu.

simultaneously with REEs sorbed on these oxides (Koeppenkastrop and De Carlo, 1993). Indeed, Mn oxides behave like Fe oxides, and as evidenced by Steinmann and Stille (2008) saturation index of goethite decrease with transport and resulting REE fractionation in the stream water.

To sum up, only the first regionalized factor corresponding to long range is representative of the conjoint variability of the elements in study. The short range variability has not proved to explain the behavior of the variables satisfactorily. The sampling scale adopted is too wide and can give sufficient information for a correlation scale of hundreds of kilometers. To be able to infer the variation at a smaller scale, further sampling on a finer spatial scale would be needed.

4.2. Rare earth elements as tracer of hydrological transfer

Research results from the past 20 years clearly show an influence of topography on stream water chemistry. Moreover several authors have proved that topography was the attribute that had the major influence on stream water chemistry (Andersson and Nyberg, 2009; Ogawa et al., 2006). The influence of topography is important because it controls the water subsurface contact time (Beven and Kirkby, 1979; Dillon and Molot, 1997; McGuire et al., 2005; Wolock et al., 1990). Topography is of great significance in hydrology, affecting soil water content, flowpaths and residence times (Nyberg, 1995), and subsequently the chemical composition of surface waters (Beven, 1986; Wolock et al., 1989). Such a feature was thus tested on REEs as previously shown by Köhler et al. (2014): in boreal catchments REE export is mostly strongly controlled by landscape type. In continental systems, percolation of rain water through the rocks will result in low-temperature chemical weathering reactions that will slowly break down the primary minerals, possibly resulting in mobility of the REEs. The chemistry of groundwater is clearly very dependent on the physico-chemical environments through which it has passed.

A focus on the Garonne and Dordogne systems, in correspondence to the Aquitaine basin characterized by higher values and anisotropy, emphasized this feature. Indeed, both river systems originate in Massif Central, where low-temperature chemical weathering of acidic magmatic rocks occurs. Moreover, topography is escarped and results in low residence time. It is highlighted in Fig. 6, where REE patterns of considered samples depicted low REE concentration and negative cerium anomaly. Positive europium anomaly can be interpreted as a result of water rock interaction with feldspar from bedrocks (i.e., basalts; Steinmann and Stille, 2008). Both river systems then encountered the Aquitaine basin, with a more flat topography with higher residence time. It results in higher REE concentrations (Fig. 6), with middle REE enriched patterns, corresponding to an organic sedimentary input. Overall, spatial variability results in REEs and organic carbon concentrations increase and a pH decrease (Fig. 7).

Wetlands would play a key role in the regulation of REE concentrations in the environment as earlier proposed (Davranche et al., 2015). Indeed REEs are released in wetland bound to colloidal organic matter as also observed in watershed or rivers (Shiller, 2010; Stolpe et al., 2013). Moreover, Fig. 7 shows the global control of dissolved REE concentrations by pH as previously highlighted for Nd by Johannesson and Burdige (2007) or Deberdt et al. (2002). Indeed, pH can significantly influence the speciation and thus the behavior of the REEs (Pourret et al., 2007; Tang and Johannesson, 2003). A decrease in pH will favor solution of the REEs and thus their transport either as organic complexes or as free ions. In Fig. 8, cerium anomaly in these two river water systems are reported as a function of the distance to the outlet.

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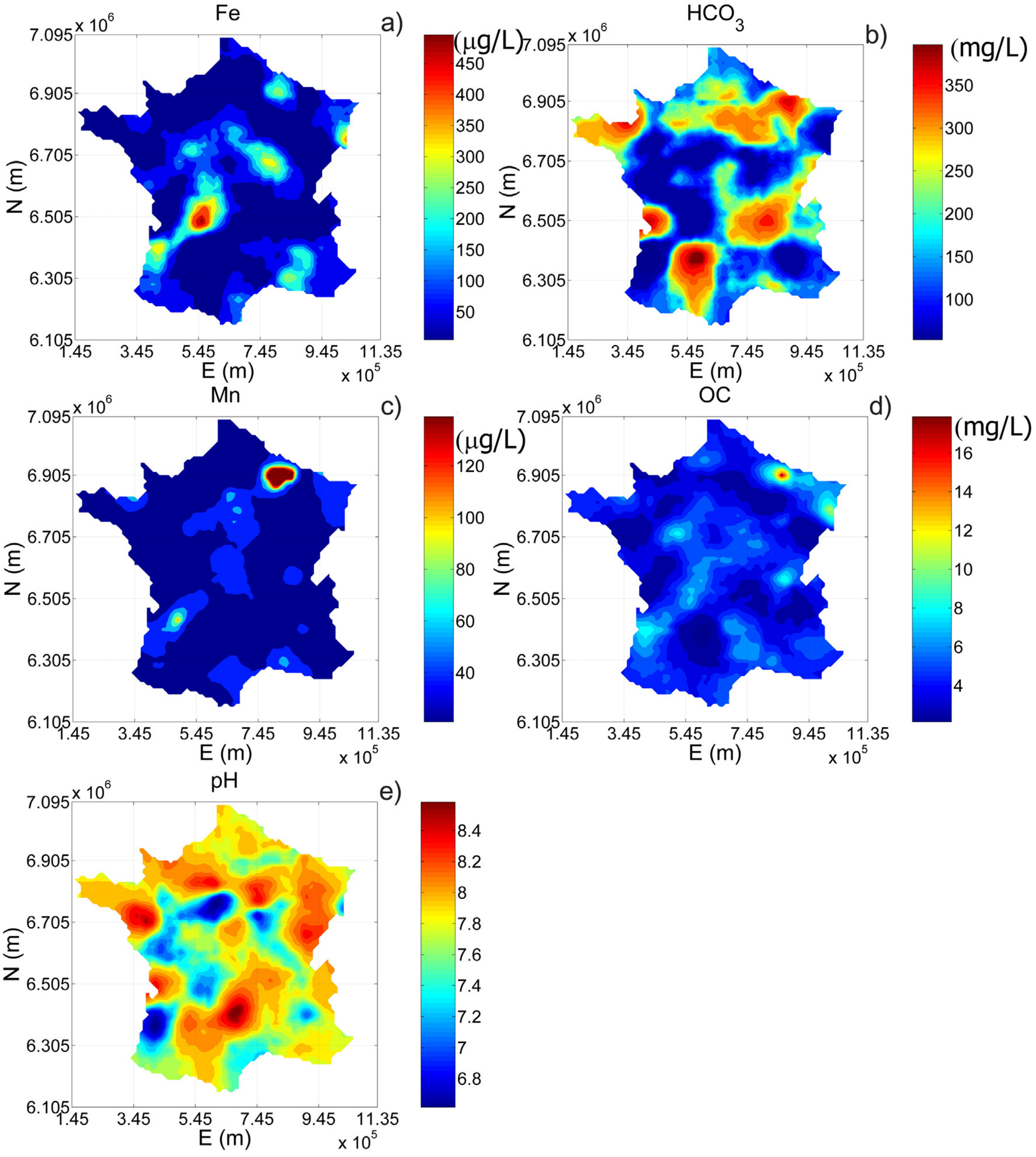

Fig. 5. Cokrigged maps of physicochemical properties (a) Fe, (b) HCO_3^-, (c) Mn, (d) organic carbon, and (e) pH.

Fig. 8 shows that the two river water systems plot along a single trend reflecting the Ce anomaly amplitude gradual reduction as the distance to the outlet decreases. It must be noted that a few points ($n = 3$) have a different behavior from this trend and correspond to more organic water (associated to wetlands). As already proposed by Pourret et al. (2010) the likely reason for the Ce anomaly amplitude gradual reduction observed mainly relies on the fact that, in low permeability aquifers, water table generally reaches organic soil horizons in bottomland domains, thus allowing incorporation of large quantities of organic colloids in the aquifer bottomland part. This feature is not seen in the aquifer upland part where the water table always remains far below the upper, organic-rich soil horizons. Considering results from this study, it appears that the general feature of shallow groundwaters flowing into aquifers developed onto low permeability bedrock (Pourret et al., 2010) can be expanded to river water systems.

5. Concluding remarks

In order to further understand REE pattern spatial distribution, the FOREGS stream dataset was processed by means of geostatistical methods. The obtained maps allow visualizing the factors which integrate REE spatial variability. Cokriging shows a similar spatial organization of REEs: higher values are observed in the Aquitaine basin, more locally in the Alpine valley corridors of the Rhone, and along some tributaries of the Loire and the Seine. A factorial cokriging was applied to investigate more deeply the different sources of variation acting in the study area. The first 2 regionalized factors have been estimated to give a synthetic description of the studied process at the different selected spatial scales. At large spatial scales (250 km) environmental parameters like Fe, carbonates, pH, are supposed be ascribed to the rock's nature (plutonic, volcanic and metamorphic versus sedimentary)

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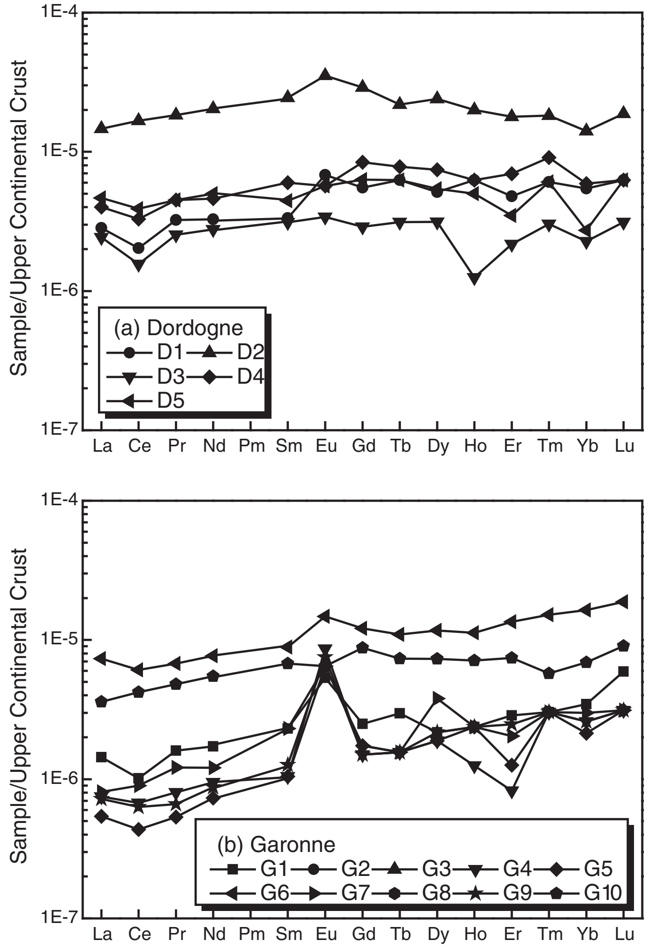

Fig. 6. Upper continental crust(UCC)-normalized REE patterns in samples from (a) Dordogne river and (b) Garonne river (UCC values are from McLennan, 2001).

or to other larger scale processes, such as hydrographic network and topography have shown to affect REE distribution. The factor kriging analysis used in this study reveals the spatial patterns of REEs in stream water. REEs are positively correlated to Fe and Mn and negatively to carbonate alkalinity and pH. At short range, only Eu and Mn weigh more, which are ascribed to the process of liberation of Mn oxides in rivers that also releases the REEs sorbed onto these oxides. This variability is discussed with some landscape factors, especially topography and upstream/downstream location. However, the short range variability cannot be explained satisfactorily by the adopted sampling as the sampling scale is too wide and can give sufficient information for a correlation scale of hundreds of km. To be able to infer the variation at a smaller scale, further sampling on a finer spatial scale would be needed.

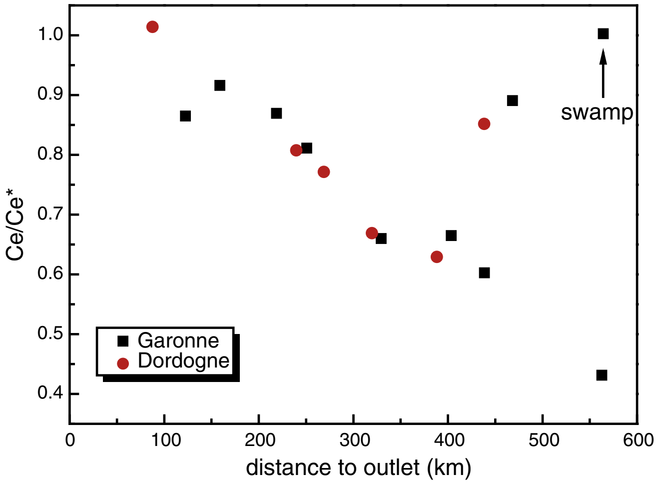

Fig. 7. Concentrations of Nd in river samples as a function of pH (Garonne–Dordogne watershed).

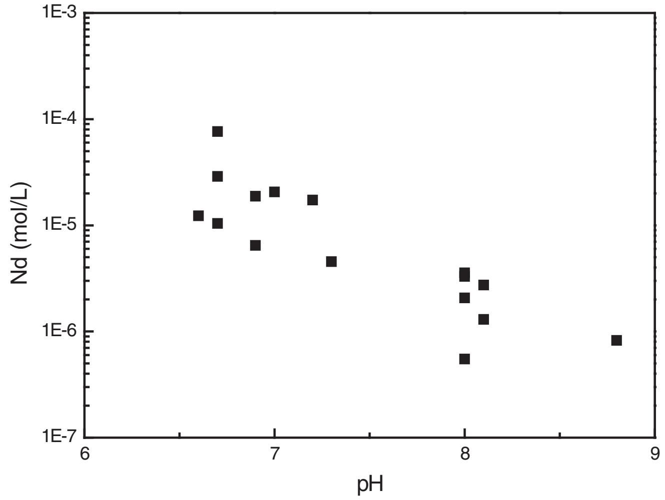

Fig. 8. Cerium anomaly as a function of distance to outlet (Garonne–Dordogne watershed).

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Annexe 4

Actes de congrès

Tuduri, J., Charles, N., Guyonnet, D., Pourret, O., Rollat, A., Escalon, V. and Planchon, M., (2014) - Rare Earth Elements in Europe and Greenland: A synthesis of lithospheric and anthropospheric potentials, 24ème Réunion des Sciences de la Terre, Pau, France, pp. 368.

Charles, N., Tuduri, J., Guyonnet, D., Pourret, O. and Melleton, J., (2014) - Rare Earth Elements in Europe and Greenland: A novel synthesis of occurrences, 1st Conference on European Rare Earth Resources, Milos Island, Greece, pp. 39-40.

Tuduri, J., Chevillard, M., Colin, S., Gloaguen, E., Gouin, J., Potel, S. and Pourret, O., (2013) - Formation of monazite-(MREE) from Paleozoic shales: role of host rock chemical composition and organic material. Mineralogical Magazine, 77(5): 2362.

Tuduri, J., Pourret, O., Gloaguen, E., Gouin, J., Potel, S., Dörr, W., Colin, S. and Chevillard, M., (2014) - U-Pb age and geochemistry of authigenic monazites of the Armorican Massif. Implications for formation of monazite-(MREE) from paleozoic shales, 24ème Réunion des Sciences de la Terre, Pau, France, pp. 342-343.

Melleton, J., Tuduri, J., Pourret, O., Bailly, L. and Gisbert, T., (2014) - Rare-earth elements enrichment of Pacific seafloor sediments: the view from volcanic islands of Polynesia, EGU 2014, 27 April – 2 May, Vienna, AU. Geophysical Research Abstracts Vol. 16, EGU2014-15804.

7.7.1 (o) Evaluating the role of hydrothermal transport of rare-metals : insights from a peralkaline granite-related skarn in the Ambohimirahavavy complex, Madagascar

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In the western world there is considerable impetus to discover new resources of rare metals (RM), i.e., REE, Zr, Y, Nb, etc. One of the principal hosts of RM deposits are peralkaline igneous intrusions. To date, there is no consensus on the mode of formation of these deposits, a key issue being whether hydrothermal processes favour economic concentrations. The Ambohimirahavavy complex hosts a rare case of HFSE-rich skarn, which offers an important opportunity to evaluate the role of hydrothermal processes on RM mineralization without having to separate it from the effects of precursor igneous concentration. The skarn forms at the contact of dykes and veinlets of peralkaline granite with the calcareous host. In addition to typical skarn minerals, aegirine and fluorite are important in the endoskarn and exoskarn, respectively, and form a fringe at the contact between the two. In the endoskarn, mineralization occurs as pseudomorphs of mostly zircon plus Nb-pyrochlore, REE-fluorocarbonates, quartz, calcite after aegirine. REE-fluorocarbonates are abundant in the exoskarn, particularly in the fringe. A fluid inclusion assemblage (FIA) occurs in quartz, calcite and diopside consists of co-existing vapor-filled and highly saline solid-bearing FI, and represents an unmixed fluid of likely orthomagmatic origin. RM-bearing phases and fluorite were identified in opened FI by SEM.
The above textural and FI evidence indicate that the RM were mobile during skarn formation. We propose that the REE were transported as Cl complexes (Williams-Jones et al. 2012, Elements) in the fluid exsolved from the granite and deposited due to the sharp increase in pH that accompanied interaction of the fluid with the marble. Presence of fluorite is consistent with the fluid interacting with a source of Ca. Other RM such as Zr were probably transported to a less extent, as they do not occur in the exoskarn.

7.7.2 (o) Les minéralisations niobifères du complexe alcalin de Crevier (Québec)

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Localisée au nord du Lac Saint-Jean dans la province de Grenville au Québec, l'intrusion alcaline de Crevier, est située sur le linéament crustal de Waswanipi-Saguenay. Cette intrusion est voisine de celle minéralisée de la mine Niobec à Saint-Honoré.
Cette intrusion est constitué de trois grandes unités : (i) une unité principale correspondant à une syénite néphélinique massive de texture variable, (ii) une syénite rubanée constituée par le recoupement de dykes de syénite néphélinique, de syénite à biotite, de syénite à biotite-carbonates, de carbonatites et de lamprophyres et (iii) d'un essaim de dykes de syénite néphélinique pegmatitique. Les chronologies relatives observées sur le terrain montrent que la première unité est intrudée par la seconde, les essaims de dykes pegmatitiques recoupant les deux premières unités. Les dykes pegmatitiques se situent au centre du complexe et sont orientés N320°. Les carbonatites sont légèrement postérieures aux pegmatites et résultent d'une immiscibilité entre liquide carbonatitique et liquide silicaté, ces deux liquides sont intrusifs dans la partie aplitique des pegmatites. Les datations de cette intrusion, réalisées par la méthode U-Pb sur zircon du faciès principal de syénite néphélinique, donnent un âge tardi-grenvillien (957,5±2,9 Ma).
Les dykes pegmatitiques représentent le potentiel économique en Nb de ce système intrusif avec une minéralisation exprimée sous forme de fluorocalciopyrochlores et fluoronatropyrochlores. Cette étude a fait ressortir l'existence de deux lignées de pyrochlores issues du processus de cristallisation fractionnée : une lignée à Nb-Ti dominant et une lignée plus tantalifère associée aux phases plus tardives.

7.7.3 (o) Rare Earth Elements in Europe and Greenland : A synthesis of lithospheric and anthropospheric potentials

Johann Tuduri[1], Nicolas Charles[1], Dominique Guyonnet[1], Olivier Pourret[2], Alain Rollat[3], Victoire Escalon[4], Mariane Planchon[4]

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Given their importance for clean energy technologies, rare earth elements (REE) are central to the energy transition in Europe. Due to stress on global markets, related in particular to the situation of Chinese monopoly, the EU-28 now consider certain REEs as critical for the development of new technologies for "carbon-free" energy generation. In response, EU-28 are developing and diversifying their supply sources, with new mining projects located outside China and efforts in the area of REE recycling. An effective supply diversification plan should consider both primary and secondary sources of REEs.
This study proposes a synthetic map of over 370 REE occurrences and deposit-types in continental Europe and Greenland, based on a global geological and metallogenic review. Most significant REE occurrences are related to the geological history of the Baltic shield and Greenland, with alkaline intrusions and carbonatites providing a huge potential (e.g. Lovozero, Norra Kärr in the Baltic shield, and the Ilímaussaq alkaline complex in South Greenland). Elsewhere in Europe, REE occurrences are relatively ubiquitous albeit of modest importance and appear in a wide variety of geodynamic settings (e.g. palaeoplacers, karstic-bauxites, REE-related to Ba-F veins ...). Moreover, in the Baltic shield, other REE-occurrences are to be considered as by-products within non-conventional deposit-types (e.g. iron-apatite Kiruna, skarns). However, progress in the understanding of the REE ore forming processes is required to help better guide exploration and make new discoveries.
Material Flow Analysis (MFA) has been also used to study in particular the flows and stocks in the EU-27 anthroposphere of selected REEs for which there is a true recycling potential (for the year 2010). If MFAs for Tb and Nd illustrate a real potential for recycling, geologic data show that if just one large exploration project outside China enters production, the criticality issue will be significantly influenced.

7.7.4 (o) L'or associé aux intrusions alcalines tardi-archéennes. Exemple de la mine Lac Bachelor, Abitibi, Canada

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Session VI-A1: REE Ore formation

Saturday, 11:40 14:00/ Hall A1

Chaired by:

Dr Daniel CASSARD

Bureau de Recherches Géologiques et Minières (BRGM), Orléans, France

Dr. George ECONOMOU

Institute of Geology and Mineral Exploration, Athens, Greece

Rare Earth Elements In Karst-Bauxites: A Novel Untapped European Resource?

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Karst-bauxite deposits form as a result of the accumulation of residual clay minerals in depressions on a karst limestone surface, and their subsequent lateritic weathering. Rare earth elements (REE) become concentrated in the bauxite deposits due to crystallisation of authigenic REE-bearing minerals, accumulation of residual phases and the adsorption of ions on clays and other mineral surfaces. All the REE are concentrated in the red mud waste generated by alumina production from bauxite through the Bayer process. Red muds thus contain on average 900 ppm REE compared with typical values of <100 ppm to ~500 ppm REE in the bauxites. Extraction of REE from red mud has been shown to be feasible although it is challenging due to the heterogeneous spatial distribution of REE in the bauxites and the need for development of appropriate processing methods. With annual European production of bauxite estimated to be approximately 3.5 million tonnes per annum, resulting in approximately 140 000 tonnes of red mud, understanding the REE resource potential of bauxites is integral to the assessment of European REE resources.

Rare Earth Elements in Europe and Greenland: A novel synthesis of occurrences

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Given their importance for clean energy technologies, rare earth elements (REE) are central to the energy transition in Europe. Due to stress on global markets, related in particular to the situation of Chinese monopoly, these materials are identified by the EU as critical. Thus, the EU aims to diversify its supply sources and to promote in particular the recycling of REEs.

But supply diversification should consider both primary and secondary sources of REEs. This study proposes a novel synthetic map of over 350 REE occurrences and deposit-types in continental Europe and Greenland, based on a global geological and metallogenic review. Most significant REE occurrences are related to the geological history of the Baltic shield and Greenland, with alkaline intrusions and carbonatites providing a huge potential (e.g. Lovozero, Norra Kärr in the Baltic shield, and the Ilímaussaq alkaline complex in South Greenland).

Elsewhere in Europe, REE occurrences are relatively ubiquitous albeit of modest importance and appear in a wide variety of geodynamic settings (e.g. palaeoplacers, karstic-bauxites, REE-related to Ba-F veins ...). Moreover, in the Baltic shield, other REE-occurrences are to be considered as by-products within non-conventional deposit-types (e.g. iron-apatite Kiruna, skarns). Consequently, progress in the understanding of REE ore-forming processes is required to define more efficient exploration guides and to make new discoveries.

The Importance Of Tectonic Setting In Assessing European Rare Earth Potential

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Rare earth element (REE) resources are commonly found associated with alkaline igneous complexes or carbonatites, or as secondary deposits derived from igneous rocks. Globally, many REE deposits occur around the margins of Archaean cratons, most in continental rift zones. Europe contains many such rift zones, which are generally younger in the south. Many of these rifts are intracontinental, whereas others are associated with the opening of oceans such as the Atlantic.

All these rift systems have the potential to host REE resources, but whereas the older provinces of northern Europe are deeply exposed, exposures in southern Europe are largely at the supracrustal level. This paper considers how an understanding of the tectonic setting of Europe's REE resources is vital to guide future exploration.

The Palaeoproterozoic Skarn-Hosted Ree Mineralisations Of Bastnäs-Type: Overview And Mineralogical – Geological Character

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The Bastnäs-type rare earth element (REE) deposits are located in the Palaeoproterozoic Bergslagen ore province in the Swedish part of the Fennoscandian

Influence of aerosols on cloud characteristics over Europe: Study with the meteorology-chemistry-radiation eulerian model.

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and Guido Visconti[1]

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Several studies demonstrated that aerosol particles play a crucial role in the climatic system, scattering the incoming radiation (direct effect) and altering cloud properties (indirect effect). Excellent efforts has been done by scientific community to represent the indirect effect in the atmospheric model, but the radiative forcing associated to indirect effect is still very uncertain.

In this study we tried to address the question: how well do the models reproduce the amplitude of aerosol indirect effects? In order to answer to the question, we used WRF/Chem model. A new parameterization for secondary organic aerosol (SOA) yield based on the volatile basis set implemented in WRF/Chem recently, has been coupled with the microphysics of clouds. The effects of this new mechanism is evaluated through the comparison of high resolution simulations on a cloud resolving domain (2 Km of resolution) against the groud-based and aircraft measurements of aerosol chemical composition and particles, and cloud microphysics, issued in the frame of European Integrated project on the Aerosol Cloud Climate and Air Quality Interaction (EUCAARI). The comparison of model results among observations suggest that discrepancies in simulation of chemical fields should be due to errors in simulated meteorological field and uncertainties in horizontal and vertical interpolation of anthropogenic emissions, in their total amount and hourly variations.

The amplitude of indirect has been calculated as $IE=\partial \mathrm{ln} re \partial \mathrm{ln} N$, where re is the cloud droplet effective radius and N aerosol particle number of each mode of log-normal distribution. Observations attribute the indirect effect to total aerosol particle number with a value of -0.22, very to theoretical value of -0.23. Instead, WRF/Chem reproduces the observed amplitude of IE, but attributes it to the particles of accumulation, while the observations indicate a strong IE due to total particle number.

The reasons of this results are under investigation.

Formation of monazite-(MREE) from paleozoic shales: Role of host rock chemical composition and organic material

Johann Tuduri[1], Matthieu Chevillard[1],
Sébastien Colin[1], Eric Gloaguen[1], Jérome Gouin[1],
Sébastien Potel[2] and Olivier Pourret[2]*

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Rare earth element (REE) distributions of stream water, normalized to upper continental crust (UCC), showed, from the source to the catchment outlet, fractionation patterns from heavy REE enriched to more flat and middle REE (MREE) enrichement, together with a progressive disappearance of a negative Ce anomaly. As a consequence, Pourret *et al.* [1] suggest that the continental shelf could be considered as a potential REE trap and thus that shelf sedimentary rocks, similar to metalliferous deep sea sediments, represent a REE potential resource and guide for their exploration. The reassessment of the REE potential of France, led us to discuss the behavior of REEs, from the continental shelf to the basin plain, using authigenic monazite occurences within ordovician shales and black shales from Britanny (France). Monazite grains (up to 2 mm in diameter) are mostly characterized by their grey color, host-rock mineral inclusions, REE_{UCC} distribution patterns enriched in MREE, low Th and U contents, lack of inherited cores, that strongly suggest authigenic crystallization during diagenesis to low grade metamorphism conditions. Chemical composition highlights zoned crystals with MREE enriched cores (up to: 10 wt% Sm_2O_3; 1.3 wt% Eu_2O_3 and 5 wt% Gd_2O_3) and light REE (LREE) enriched rims. Thus grain cores are characterized by negative and low values of $\log[(La/Sm)_{UCC}]$ and high values of Eu whereas rims have slightly negative to positive values of $\log[(La/Sm)_{UCC}]$ with low Eu concentrations. Grey monazite REE_{UCC} patterns also reflect the abundance of these elements in shales and black shales. Indeed, at near neutral to alkaline pH, monazite evidenced MREE enriched patterns directly linked to organic matter (OM) content, whereas at alkaline pH, REE speciation is mainly driven by carbonate complexation, resulting in the formation of the LREE enriched monazite. This latter hypothesis will be further tested and reinforced by analysing OM fractions of shales and black shales. Eventually, such monazites were later concentrated within placers @ 2 kg/t.

[1] Pourret *et al*. (2012) *Mineralogical Magazine* 76 , 2247.

Les données thermobarométriques suggèrent des conditions au pic du métamorphisme de 5-6 kbar et 800-850˚C. Les données géochronologiques obtenues sur monazite et zircon permettront de contraindre ce contexte tectono-métamorphique, les phénomènes de pré-concentration en uranium et d'altération plus tardive.

7.3.10 (o) Comment la monazite peut enregistrer et préserver l'âge d'événements métamorphiques successifs de haut grade : l'exemple des métapélites à Grt-Ky du Rhodope Central (Bulgarie, Grèce)

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Le faible taux de diffusion du Pb dans la structure cristalline de la monazite, même à température élevée, en fait un géochronomètre robuste susceptible de préserver les âges d'événements métamorphiques successifs. Nous présentons des données texturales, chimiques et des âges U-Th-Pb in situ dans les monazites des métapélites à Grt-Ky des zones de cisaillement de Chepelare (Bulgarie) et Nestos (Grèce) dans le Rhodope central. Les échantillons étudiés ont subi deux épisodes de métamorphisme à haute température : le premier est responsable d'une fusion partielle anhydre dans le faciès des granulites au Mésozoïque, le second implique une fusion partielle hydratée au Cénozoïque. Une déformation ductile intense en présence de fluides est visible dans la majorité des échantillons. La monazite est présente dans la matrice foliée ainsi qu'en inclusion dans le grenat et le disthène. Les monazites de la matrice présentent des évidences de dissolution-recristallisation en présence de fluides. La majeure partie des grains est formée de domaines pauvres en Y donnant des âges entre 115 et 165 Ma. Des domaines riches en Y présentant des âges cénozoïques forment les bordures des grains matriciels ou de petits grains satellites entourant les grains mésozoïques. Les monazites cénozoïques cristallisent au dépend des monazites mésozoïques et incorporent simultanément l'Y provenant de la dissolution partielle du grenat. Dans les deux zones de cisaillement, la croissance des monazites cénozoïques est datée à 36 Ma. Des âges identiques ont été obtenus dans les leucosomes et pegmatites des gneiss migmatitiques environnants indiquant que les fluides responsables de la précipitation des monazites cénozoïques provenaient probablement de la cristallisation de liquides anatectiques adjacents. Ces résultats montrent l'efficacité des processus de dissolution-précipitation dynamique qui favorisent la cristallisation d'une nouvelle génération de monazite pendant la déformation à 36 Ma.

7.3.11 (p) Insights from monazite and allanite petrochronology in metasediments from Central Alps

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Monazite and allanite are two REE-minerals that are powerful U-Th-Pb geochronometers of metamorphic crystallization, especially for relatively low T metamorphic conditions (typically T<500˚C). In both minerals, solid diffusion is inefficient up to elevated temperature, and U-Th-Pb ages are attributed to (re)crystallization episodes. Correct age interpretations require identification of the processes and conditions under which REE-mineral (re)crystallized. Combining petrology and geochronology (petrochronology) of REE-minerals is hence vital for correlating age with physic-chemical conditions.
In metasediments and veins of the Central Alps, petrochronology of REE-minerals gave precious insights on successive episodes on monazite and allanite crystallization depending on temperature, fluid, fO2 and deformation. Along the very well studied metamorphic profile of the Central Alps, a general metamorphic sequence Monazite Þ Allanite Þ Monazite was identified. Combining in-situ high resolution U-Th-Pb dating of the two minerals enable to fix temporal anchors on the entire orogenic cycle : accretion, metamorphic peak and exhumation. Ages obtained in different part of the Central Alps indicate a diachronism with younger ages found towards the North.

7.3.12 (p) Behaviour of monazite during ultra-high temperature metamorphism

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Ultra-high temperature (UHT) metamorphism (T > 900˚C) reflects the most extreme thermal conditions that the continental crust can achieve. It has been proven that monazite is stable under such conditions in rocks of appropriate bulk composition, however its petrogenesis and relationship with the main silicate rock-forming minerals is still poorly understood. The Proterozoic province of Rogaland (South Norway) exhibits typical UHT mineral assemblage such as osumilite + orthopyroxene + hercynite + garnet along with abundant monazite. In the osumilite gneiss two generations of monazite may be distinguished on the basis of their petrostructural position and their Y and Th contents. These two monazite generations may be correlated with contrasted mineralogical paragenesis which have been investigated using P-T-X phase diagrams in the Na2O-CaO-K2O-FeO-MgO-Al2O3-SiO2-H2O system. The type-I monazite is shielded into porphyroblastic garnet enclosing sillimanite and biotite interpreted as relicts of a MT-MP metamorphic event. Type-I monazite displays concentric BSE zoning with low Y concentration, moderate ThO2 content and rare inclusions of zircon. Besides, type-II monazite corresponds to rather large (up to 850 μm) crystals and is found within the M2 decomposition products of garnet consisting of high Al2O3 orthopyroxene blasts and osumilite ?hercynite bands equilibrated around 980-1030 ˚C and 4-6 kbar at dry and moderately oxidizing conditions. This second monazite type shows a patchy BSE zoning with very high content of ThO2 and abundant inclusions of peak temperature hercynite along with magnetite, pyrite, pyrrhotite as well as zircon. Further isotopic study in these monazite crystals will investigate whether the U-Pb and Th-Pb systems can record the age of the UHT peak-temperature.

7.3.13 (p) U-Pb age and geochemistry of authigenic monazites of the Armorican Massif. Implications for formation of monazite-(MREE) from paleozoic shales

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Rare earth element (REE) distributions of stream water, normalized to upper continental crust (UCC), showed, from the source to the catchment outlet, fractionation patterns from heavy REE enriched to more flat and middle REE (MREE) enrichement, together with a progressive disappearance of a negative Ce anomaly. As a consequence, it is suggested that the continental shelf could be considered as a potential trap for MREE resources, similar to metalliferous deep sea sediments, defining new guide for offshore exploration. The reassessment of the REE potential of France, led us to discuss the behavior of REEs, from the continental shelf to the basin plain, using authigenic monazite occurences within ordovician shales and black shales from Britanny (France). Monazite grains (up to 2 mm in diameter) are mostly characterized by their grey color, host-rock mineral inclusions, REEUCC distribution patterns enriched in MREE, low Th and U contents, lack of inherited cores. Chemical composition highlights zoned crystals with MREE enriched cores (up to : 10 wt% Sm2O3 ; 1.3 wt% Eu2O3 and 5 wt% Gd2O3) and light REE (LREE) enriched rims. Thus grain cores are characterized by negative and low values of log[(La/Sm)UCC] and high values of Eu whereas rims have slightly negative to positive values of log[(La/Sm)UCC] with low Eu concentrations. REEUCC patterns in grey monazite also reflect the abundance of these elements in shales and black shales. Indeed, at near neutral to alkaline pH, monazite evidenced MREE enriched patterns directly linked to organic matter (OM) content, whereas at alkaline pH, REE speciation is mainly driven by carbonate complexation, resulting in the formation of the LREE enriched monazite. These data strongly suggest authigenic crystallization of monazite during deep diagenesis to very low grade metamorphism conditions as highlighted by U/Pb monazite age dating by TIMS at 384 ± 1.6 Ma. Eventually, such monazites were later concentrated within placers @ 2 kg/t.

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Rare-earth elements enrichment of Pacific seafloor sediments: the view from volcanic islands of Polynesia

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Rare-earth elements (REEs) are key metals for «green» technologies such as energy saving lamps or permanent magnets used in, e.g., wind turbines, hard disk drives, portable phone or electric or hybrid vehicles. Since several years, world demand for these metals is therefore drastically increasing. The quasi-monopolistic position of China, which produces around 95 % of global REEs production, generates risks for the industries that depend on a secure supply of REEs. In response, countries are developing and diversifying their supply sources, with new mining projects located outside China and efforts in the area of REEs recycling.

Most of these projects focus on deposits related to carbonatites and alkaline-peralkaline magmatism, which are generally enriched in light REEs (LREEs) compared to the heavy REEs (HREEs)-enriched deposits of the ion-adsorption types, located in southern China. However, a recent study revealed new valuable resources corresponding to seafloor sediments located in the south-eastern and north-central Pacific. The deep-sea mud described by these authors show a higher HREE/LREE ratio than ion-adsorption deposits, a feature which significantly increases their economic interest. The authors suggest mid-ocean ridge hydrothermal activity as an explanation to this anomalous enrichment.

However, several contributions have documented considerable REEs enrichment in basalts and peridotitic xenoliths from French Polynesia. Several arguments have been exposed in favour of a supergene origin, with a short migration, suggesting that REEs were collected from weathered basalts. The Tahaa volcanic island (Sous-le-Vent Island, Society Archipelago, French Polynesia) is the first location where such enrichment has been described. New petrographic and mineralogical investigations confirm a supergene mobilization of this abnormal occurrence. REE-bearing minerals (mainly phosphates of the rhabdophane group) are primarily located within basalt vesicles but also in crack that cross-cut the calcite filling the vesicles or the volcanic glass. They are also closely associated with Ni-Mg bearing phyllosilicates, which appear to nucleate from alteration of olivine and clinopyroxenes. Further investigations are done to evidence and confirm an anterior magmatic enrichment.

On the basis of these observations, we believe that the anomalous enrichment observed in seafloor sediments could derive from abnormally-rich provinces corresponding to aerial basaltic formations from oceanic islands primarily enriched during weathering processes (Melleton et al., 2014).

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