UNIVERSITÉ DU QUÉBEC À MONTRÉAL

THÈSE PRÉSENTÉE À
L'UNIVERSITÉ DU QUÉBEC À CHICOUTIMI
COMME EXIGENCE PARTIELLE
DU DOCTORAT EN RESSOURCES MINÉRALES
OFFERT À
L'UNIVERSITÉ DU QUÉBEC À MONTRÉAL
EN VERTU D'UN PROTOCOLE D'ENTENTE
AVEC
L'UNIVERSITÉ DU QUÉBEC À CHICOUTIMI

PAR

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# LES ISOTOPES DU Pb EN MÉTALLOGÉNIE: CHRONOMÈTRES ET TRACEURS DU MODE DE FORMATION DE GÎTES DE Mo, Au, Ni, Cu ET Pb DANS LES PROVINCES DU SUPÉRIEUR ET DE GRENVILLE DU BOUCLIER CANADIEN

NOVEMBRE 1992

CETTE THÈSE A ÉTÉ RÉALISÉE
À L'UNIVERSITÉ DU QUÉBEC À MONTRÉAL
DANS LE CADRE DU PROGRAMME
DE DOCTORAT EN RESSOURCES MINÉRALES
DE L'UNIVERSITÉ DU QUÉBEC À CHICOUTIMI
EXTENSIONNÉ À L'UNIVERSITÉ DU QUÉBEC À MONTRÉAL

# RESUME

La composition isotopique du Pb de divers minéraux présents dans des gîtes métallifères (Mo, Au, Ni, Cu, Pb) du Bouclier canadien ainsi que dans les roches encaissant la minéralisation a été déterminée dans le but de dater directement les minéraux porteurs du minerai et caractériser la nature des régions-sources des métaux.

Des feldspaths potassiques provenant de trente massifs granitoïdes d'âge archéen, représentatifs des différentes suites intrusives des sous-provinces de l'Abitibi et du Pontiac ont été analysés afin d'estimer la composition isotopique initiale du Pb de ces roches. Les gneiss montrent une grande variation de composition initiale témoignant de la présence de réservoirs isotopiques très radiogéniques à l'Archéen dans la sous-province de Pontiac ainsi que le long de sa frontière sud avec la zone tectonique du Front de Grenville. Les intrusions granitoïdes possèdent également une grande variation du rapport $^{207}Pb/^{204}Pb$, celui-ci variant depuis des compositions typiques des roches mafiques provenant de la fusion du manteau vers celles des formations de fer sédimentaires. Les roches intrusives mises en place entre 2.72 et 2.68 Ga proviennent principalement de sources mantelliques juvéniles alors que les intrusions âgées de 2.68 à 2.64 Ga résultent plutôt de la fusion de segments de croûte évoluée. De façon générale, les roches granitoïdes de la sous-province de l'Abitibi ont des compositions isotopiques initiales de Pb moins radiogéniques que celles des roches granitoïdes du Pontiac, ce qui suggère que ces deux sous-provinces représentent des segments de croûte distincts juxtaposés tectoniquement.

La molybdénite et ses minéraux associés provenant de dix localités dans diverses provinces archéennes du Supérieur et dans la province de Grenville ont été analysés pour la composition isotopique du Pb. La molybdénite a fait l'objet d'essais analytiques ayant pour but de créer artificiellement un étalement des points dans le diagramme isochrone du Pb à partir d'un seul cristal. Des lessivages successifs à l'acide sur un même échantillon ont démontré qu'il est possible d'extraire, préférentiellement au plomb commun initial, le Pb radiogénique provenant de la désintégration *in situ* de l'uranium et du thorium. La composition des lessivats et des résidus d'échantillons de molybdénite ainsi que celle des minéraux associés (principalement le feldspath potassique) s'alignent généralement bien dans le diagramme isochrone de Pb, livrant des âges compatibles avec la géochronologie connue des régions d'étude. Les échantillons archéens (ca. 2.6 Ga) livrent des erreurs variant de 5 à 30 Ma alors que l'erreur sur l'âge des échantillons protérozoïques (1.3 à 0.9 Ga) n'est jamais inférieure à 50 Ma. Un milliard d'années représente donc la limite minimale de l'application de la méthode. Certaines des molybdénites échantillonnées dans les sous-provinces de Wabigoon et de l'Abitibi ont livré des âges nettement plus jeunes que ceux des roches encaissantes. Dans ce cas, la composition du feldspath potassique provenant des roches minéralisées se place systématiquement sous la droite définie par la molybdénite dans le diagramme isochrone. Ceci suggère une remobilisation hydrothermale du minerai, entraînant une remise à zéro du système U-Pb dans la molybdénite. Les bilans géochimiques indiquent une perte de 30 à 40% d'uranium relativement au Pb lors de ces perturbations. Les rapports isotopiques de Pb des lessivats et des résidus de molybdénite sont en corrélation positive dans le diagramme $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ et s'alignent selon des droites correspondant à des rapports Th/U variant de 0.6 à 2. Ces faibles valeurs, comparativement à celles estimées pour la croûte continentale moyenne (Th/U ~ 4.6), reflètent soit un fort fractionnement de U et Th entre les fluides minéralisateurs et la molybdénite, soit une caractéristique des fluides magmatiques évolués. Sept échantillons de molybdénite provenant du bloc tectonique de Lacorne dans le sud de l'Abitibi ont été analysés pour leur concentration en uranium. Tous les échantillons se place au-dessus de la courbe Concordia, témoignant d'une perte en uranium

relative au Pb de 50 à 95%. Les âges Pb-Pb obtenus sur les molybdénites doivent donc être considérés comme des âges maxima. Cette perte systématique de l'élément père du système U-Pb n'est pas sans rappeler le comportement du système Re-Os dans la molybdénite. Ces pertes pourraient être occasionnées par des changements des conditions de Eh et pH du milieu.

Différents minéraux provenant des gisements d'or de Silidor et de Launay du sud de l'Abitibi ont été analysés pour la composition isotopique du Pb. La pyrite (porteuse d'or), la chlorite et le quartz, provenant d'une veine de quartz aurifère de la mine Silidor, définissent une droite dans le diagramme isochrone de Pb, correspondant à un âge de 2563±12 Ma, qui est interprété comme étant l'âge de cristallisation du corps minéralisé. La molybdénite, la pyrite, l'hématite et les feldspaths de trois échantillons provenant de la zone minéralisée du gîte de Launay sont en corrélation positive dans le diagramme isochrone de Pb, selon une droite correspondant à un âge de 2.6 Ga. Cependant, la dispersion des points de part et d'autre de la droite obtenue excède celle due à la précision analytique. Les données présentent une meilleure corrélation lorsque la molybdénite est omise et les points s'alignent selon une droite correspondant à un âge de 2612±36 Ma. La composition isotopique des feldspaths potassiques provenant de la zone minéralisée de Launay ainsi que celle du quartz de Silidor sont nettement plus radiogéniques que celle des feldspaths provenant des roches encaissant la minéralisation, suggérant des sources de Pb distinctes. Les âges Pb-Pb obtenus pour ces deux gisements d'or sont en accord avec ceux livrés par d'autres géochronomètres, tels que U-Pb, Ar-Ar et Sm-Nd pour différents gîtes d'or de l'Abitibi se situant le long de la faille Cadillac-Larder-Lake. L'évidence d'activité hydrothermale entre 2.61 et 2.55 Ga à plus de 50 km au nord de cette faille supporte l'idée d'un métamorphisme régional à cette époque.

Les données isotopiques de Pb pour les gîtes d'or de la province du Supérieur, provenant de notre étude et de la littérature, sont comparées aux compositions isotopiques initiales du Pb des granitoïdes des sous-provinces de l'Abitibi et du Pontiac. Les veines de quartz aurifères encaissées dans les assemblages volcano-sédimentaires possèdent des compositions variées couvrant toute la gamme des compositions, depuis celles du domaine mantellique à celles du domaine crustal. Les minéralisations aurifères contenues à l'intérieur des roches granitoïdes possèdent généralement des compositions plus radiogéniques, témoignant d'une source à caractère plutôt crustale.

Quatre gîtes de Ni, Cu et Pb d'affiliation volcanique localisés dans la ceinture de roches vertes archéennes de Baby-Belleterre dans le sud de la sous-province de Pontiac ont été échantillonnés dans le but de déterminer la composition isotopique du Pb des minéraux constituants. Les sulfures et les silicates du gîte de Ni-Cu de Kerr Adisson définissent une droite dans le diagramme isochrone du Pb, qui correspond à un âge de 2694±30 Ma, et à un rapport $^{238}U/^{204}Pb$ ($\mu_1$) de la région-source égale à 7.8, suggérant une origine mantellique por les fluides minéralisateurs. L'âge et la valeur de $\mu_1$ du gîte de Kerr Adisson sont identiques à ceux trouvés pour les coulées de laves komatiitiques et les minéralisations associées aux roches mafiques et ultramafiques de la ceinture de l'Abitibi, indiquant une origine commune possible por les séquences supracrustales des deux sous-provinces. Les trois autres minéralisations ont livré des compositions isotopiques de Pb compatibles avec des âges protérozoïques plutôt qu'archéens. Des âges Pb-Pb de 2172±17 Ma et de 2210±40 Ma sont définis respectivement par les sulfures du prospect de Patry (Cu) et des mines Lorraine (Cu-Ni) et Wright (Pb). Ces âges sont interprétés comme des âges de remobilisation des sulfures par des fluides hydrothermaux, engendrés par la mise en place contemporaine de dykes de diabase pendant le Protérozoïque.

## REMERCIEMENTS

Ce travail n'aurait pu s'achever sans la collaboration de plusieurs personnes. Je voudrais d'abord remercier mes directeurs de thèse, Clément Gariépy et Nuno Machado, qui m'ont guidé lors de mes travaux de laboratoire et lors de la rédaction de ce manuscrit. Je voudrais aussi remercier le personnel technique du GEOTOP et du Département des Sciences de la Terre, Francine Robert, Raynald Lapointe, Bassam Ghaleb, Guy Robert et Michelle Laithier, les assistants de recherche Martin Parent, Sofie Tremblay, Christian Dicaire et Sylvain Vallières ainsi que les stagiaires post-doctoraux Jean David, Bill Davis et Dave Scott pour leur soutien et leurs conseils au laboratoire et leur aide sur le terrain. La participation de Maurice Rive, du Ministère de l'Energie et des Ressources du Québec, aux campagnes d'échantillonnage sur le terrain fut grandement appréciée. Quelques échantillons m'ont été donnés par Michel Jébrak, Michel Gauthier et Charles Normand; je les en remercie grandement.

Cette thèse fut subventionnée par différents organismes: Fonds pour la Formation de Chercheurs et l'Aide à la Recherche du Québec, le Conseil de Recherche en Sciences Naturelles et en Génie du Canada et Energie Mines et Ressources du Canada. Je les remercie pour la confiance qu'ils ont eu à mon égard.

Je voudrais finalement remercier ma compagne Caroline Guilmette pour son soutien et ses encouragements à travers toute la durée de mes travaux, ainsi que mon fils de 20 mois, qui m'a laissé quelques heures de sommeil pendant ces courtes nuits.

Je dédie ce travail à la mémoire de mon père qui nous a quitté au moment où je débutais ce travail, en octobre 1989.

# TABLE DES MATIERES

# INTRODUCTION

Des études géochronologiques récentes portant sur les gîtes métallifères de la Province du Supérieur du Bouclier canadien (en particulier les concentrations aurifères) démontrent qu'il est possible de dater précisément, par la méthode U-Pb, des minéraux accessoires présents dans les zones d'altération des minéralisations (Corfu et Muir 1989; Jemielita et al. 1990; Schandl et al. 1990; Wong et al. 1991). Cependant, pour une même région et voire une même mine, différents minéraux comme le zircon, la monazite, la titanite et le rutile, qui sont tous considérés contemporains des phases porteuses du minerai, ont livré des âges U-Pb variant de 2680 Ma pour le zircon (Claoué-Long et al. 1990) à 2600 Ma pour le rutile (Wong et al. 1991). Il est important de constater que cette fourchette d'âges est nettement plus jeune que celle obtenue pour les roches encaissantes de ces minéralisations qui varie de 2720 Ma à 2690 Ma (Corfu et Muir 1989; Wong et al. 1991; Mortensen 1992a, b). D'autres études portant sur la datation des minéraux d'altération associés aux zones minéralisées ont démontré qu'ils se sont formés tardivement par rapport aux roches encaissantes. Kerrich et al. (1987), Hanes et al. (1989) et Anglin (1990), entre autres, rapportent des âges Ar-Ar et Sm-Nd pour ces minéraux variant de 2600 Ma à 2550 Ma, une fourchette d'âges proche de l'âge obtenu pour le rutile. Il est difficile d'identifier lequel ou lesquels de ces minéraux accessoires ont co-précipité avec le minerai, mais tous les âges enregistrés par les différents systèmes isotopiques indiquent que plusieurs "événements minéralisateurs" se sont produit 10 à 90 Ma après l'activité magmatique des ceintures de roches vertes de la Province du Supérieur.

La connaissance de l'âge et de la source des minéralisations s'avèrent donc essentiels à la bonne compréhension du mode de formation des gîtes métallifères. Les traceurs géochimiques comme les isotopes du Pb représentent un outil privilégié pour ce type d'étude parce que: (1) le Pb est toujours présent en traces dans les minéraux porteurs de la minéralisation; (2) la composition isotopique initiale des minéraux donne accès au rapport en temps intégré $^{238}U/^{204}Pb$ ($\mu_1$) des roches sources; (3) la courte demie-vie de $^{235}U$ permet la formation de réservoirs possédant des compositions isotopiques distinctes à l'Archéen; et (4) l'uranium présent en traces dans certains minéraux permet la croissance *in situ* de Pb radiogénique qui peut être utilisé pour construire des isochrones Pb-Pb.

Ce travail porte donc sur l'étude des systèmes Pb-Pb et U-Pb de certains gîtes de molybdène, or, cuivre, nickel et plomb, ainsi que leurs roches encaissantes, dans les sous-provinces de l'Abitibi et du Pontiac de la province du Supérieur. La thèse est présentée sous forme d'articles scientifiques constituant cinq chapitres.

Le chapitre 1 présente la composition isotopique du Pb des différents réservoirs présents dans les sous-provinces de l'Abitibi et du Pontiac. Pour ce faire, des feldspaths potassiques provenant de 30 granitoïdes représentatifs des différentes suites intrusives de ces sous-provinces (Rive et al. 1990) ont été analysés. Comme plus de la moitié de ces plutons ont été datés de façon indépendante par la méthode U-Pb, il fut possible d'établir une évolution temporelle de la composition des sources magmatiques. La composition isotopique des différents réservoirs de Pb présentée dans ce chapitre est par la suite utilisée comme grille de référence dans les chapitres suivants portant sur les concentrations métallifères. Ce chapitre a été accepté pour publication par la revue Chemical Geology.

Le chapitre 2 porte sur le développement d'une méthode de datation directe des sulfures, à l'aide des isotopes du Pb. Dans la littérature, les droites isochrones Pb-Pb construites à partir des données obtenues sur les phases sulfurées livrent généralement des âges comparables à ceux obtenus par d'autres minéraux à l'aide de différents systèmes isotopiques. Par contre, les âges Pb-Pb sont souvent peu précis, possédant typiquement des erreurs de l'ordre de 40 à 100 Ma pour des sulfures archéens. Dans certains cas, ces erreurs peuvent être attribuées à l'ouverture du système U-Pb dans les minéraux. La faible dispersion des points dans le diagramme isochrone est cependant la principale raison de ces larges erreurs. Dans le but d'augmenter l'étalement des rapports isotopiques du Pb dans les diagrammes isochrones, Deloule et al. (1989) ont utilisé des lessivages à l'acide sur différentes phases sulfurées. Les résultats démontrent que la composition des lessivats est plus radiogénique que celle du résidu et sont interprétés comme reflétant un lessivage préférentiel du Pb radiogénique se trouvant dans des sites cristallins endommagés par la désintégration radioactive de l'uranium. Les lessivages les plus efficaces ont été faits sur des cristaux de molybdénite d'âge archéen, dont les lessivats ont livré des rapports $^{206}Pb/^{204}Pb$ excédant 50. Ce chapitre a donc pour but de décrire une technique de lessivage à l'acide (Technique de Dissolution Différentielle: TDD) et d'évaluer son potentiel géochronologique, en utilisant la molybdénite. Des résultats sont présentés pour six gîtes de molybdène précambriens encaissés dans des pegmatites, des granites et des skarns des provinces du Supérieur et de Grenville.

Le chapitre 3 constitue la mise en application de la TDD sur quelques-unes des concentrations à molybdène les plus importantes du sud de la ceinture de roches vertes de l'Abitibi. Ces minéralisations proviennent du bloc tectonique de Lacorne et sont associées à des granites à deux micas post-tectoniques. Bien que les âges obtenus par TDD sur des sulfures provenant de différentes localités de l'Abitibi soient en accord avec la géochronologie connue de la région (Deloule et al. 1989), une étude du système Re-Os sur une molybdénite provenant du pluton de Lacorne démontre que ce couple isotopique est ou a été en système ouvert depuis la formation du cristal (Luck et Allègre 1982), ce dernier livrant un âge Re-Os moyen de 6.5 Ga. Cet âge est interprété par Luck et Allègre (1982) comme reflétant une perte en Re lors d'événements thermiques postérieurs à la cristallisation. Il semble en effet que le système Re-Os s'ouvre facilement dans la molybdénite. Une perte de plus de 70% de Re est nécessaire pour expliquer des âges Re-Os de cristaux de molybdénite provenant de la côte ouest de l'Amérique du nord, qui sont plus vieux que ceux des roches encaissant la minéralisation (Luck et al. 1983). Le but de ce chapitre est donc de vérifier si le système U-Pb est demeuré clos dans la molybdénite tout au long de l'histoire du minéral. Les cristaux de molybdénite ayant livré les compositions isotopiques de Pb les plus radiogéniques ont été analysés pour leur concentration en uranium et en Pb. La position des rapports Pb/U dans le diagramme Concordia nous indiquera si le système U-Pb est resté clos ou non.

Le chapitre 4 présente la composition isotopique du Pb de différents minéraux retrouvés dans deux gîtes d'or du sud de l'Abitibi, la mine Silidor et le prospect de Launay.

Pour faire suite aux récentes études géochronologiques sur les minéralisations aurifères, différents modèles concernant l'origine des fluides minéralisateurs ont été développés. Le modèle magmatique propose que, pour certains gisements, l'or provient de la même source magmatique que les intrusions felsiques encaissantes (Burrows et Spooner 1989; Cameron et Hattori 1987). Par contre, Groves et Phillips (1987) ont proposé que les fluides minéralisateurs soient générés par un métamorphisme prograde à la base des ceintures de roches vertes. Finalement, un troisième modèle attribue la formation des fluides à des processus de grandes profondeurs, incluant le dégazage mantellique de $CO_2$, la granulitisation et la fusion partielle de la croûte inférieure (Cameron 1988; Colvine et al. 1988; Fyon et al. 1989; Perring et al. 1989). Ce chapitre a pour but de dater directement la minéralisation aurifère en analysant non seulement les minéraux associés au minerai mais aussi les minéraux porteurs d'or. Les phases contenant de l'uranium en traces ont subit des traitements à l'acide (TDD) dans le but d'augmenter l'étalement des points dans le diagramme Pb-Pb et ainsi d'améliorer la précision de l'âge. La composition isotopique du Pb des minéralisations est comparée à celle d'autres gisements d'or de la Province du Supérieur, ainsi qu'à celle des granitoïdes des sous-provinces de l'Abitibi et du Pontiac, dans le but de vérifier la pertinence des modèles génétiques proposés. Cet article a été soumis à la revue Economic Geology.

Le chapitre 5 présente la composition isotopique du Pb de certains gîtes de Ni, Cu et Pb provenant de la ceinture de roches vertes de Baby-Belleterre dans le sud de la sous-province du Pontiac. Cette ceinture est très semblable à celle de l'Abitibi, tant à ce qui a trait aux assemblages lithologiques qu'aux minéralisations. La ceinture volcanique de Baby-Belleterre peut être interprétée comme représentant un klippe de roches supracrustales reliées aux roches ignées d'âge comparable de l'Abitibi (Rive et al. 1990). Des isochrones Pb-Pb sur minéraux, utilisant la TDD, ont été déterminés pour quatre gîtes d'affiliation volcanique de la ceinture de Baby-Belleterre dans le but de: (1) déterminer l'âge de formation des gisements, (2) caractériser isotopiquement les régions-sources des métaux, (3) comparer la composition isotopique du Pb des minéralisations de la ceinture de Baby-Belleterre avec celle des minéralisations de la ceinture de l'Abitibi, et (4) placer les "événements minéralisateurs" dans un cadre tectonique. Cet article a été accepté pour publication par la revue Economic Geology.

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# Pb isotopic geochemistry of granitoids and gneisses from the late Archean Pontiac and Abitibi Subprovinces of Canada

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Accepted for publication by *Chemical Geology*

ABSTRACT

Initial Pb isotopic compositions were determined on K-feldspars for thirty granitoid plutons and gneiss complexes in the Abitibi and the Pontiac Subprovinces of Canada. The gneisses cover a wide spectrum of initial Pb isotopic compositions and undoubtedly demonstrate that very radiogenic reservoirs were present in the Pontiac Subprovince and along its southern boundary with the Grenville Province in the late Archean. The granitoid rocks also define a large spectrum, covering 0.3 unit of the $^{207}Pb/^{204}Pb$ ratio, ranging from compositions typical of mafic mantle melts to those of sedimentary banded iron formations.

The older intrusives emplaced between 2.72 and 2.68 Ga were principally derived from juvenile mantle sources. They may have been formed in a volcanic arc environment, but they still frequently record the signature of crustal precursors which may have been represented by subducted sediments or by older assimilated crustal components. A sharp change in the provenance of the granitoid magmas occurred close to 2.68 Ga, an age that also corresponds to an episode of alkaline activity and fault-related sedimentation. For the following 40 Ma, magmatism chiefly resulted from melting of crustal precursors in a thickened crustal lithosphere. The Pb isotopic compositions of these crustal melts demonstrate that the basement of the Pontiac Subprovince contains a major component of rocks older than 3.0 Ga. In comparison, the Abitibi Subprovince may not contain basement components older than 2.9 Ga, or else they represent a negligible fraction of the crust. This supports the concept that the Abitibi and Pontiac Subprovinces formed as discrete crustal segments tectonically juxtaposed. Finally, the Grenville Front tectonic zone was metamorphosed and partially melted in the late Archean and is probably the deep crustal equivalent of the Pontiac Subprovince.

## 1. Introduction

The formation of juvenile continental crust in Archean cratons follows a similar pattern in many regions of the world: it begins with the eruption of thick mafic volcanic piles and is followed ~30 Ma later by the intrusion of voluminous granitoid bodies (Arndt, 1992). Archean intrusions cover a wide lithological spectrum and they may have formed in response to a variety of tectonic processes. For example, differentiated mafic bodies may represent juvenile magmas directly derived from the mantle, tonalite-trondhjemite complexes associated to calc-alkaline volcanism may correspond to volcanic arc remnants while S-type granites may be formed by crustal anatexis in response to regional thrusting and burial of sedimentary rocks. Thus, distinguishing the immediate source of granitoid bodies from their ultimate origin in the mantle may be helpful to unravel the tectonic development of Archean orogens.

Radiogenic isotope tracers are now widely used to decipher the origin of magma series. The tracers are especially useful when the isotopic compositions of the potential end-members are well characterized and when a precise time frame of reference is available. However, the resolution of any isotopic tracer is limited by the degree of fractionation of the parent/daughter ratio and by the time scale of the crustal recycling processes. The U-Pb system is particularly well suited to study the origin of Archean magmas because mantle melts stored in the continental crust have U/Pb ratios significantly larger than their source, such that the Archean crust rapidly developed radiogenic $^{207}Pb/^{204}Pb$ ratios because of the relatively short half-life of the parent $^{235}U$ isotope.

New initial Pb isotopic compositions are reported for 30 late Archean granitoid bodies and gneiss complexes of the central Abitibi and the Pontiac Subprovinces of Canada. This area has been selected because several of the granitoids and gneisses have been independently dated with the U-Pb concordia method (Frarey and Krogh, 1986; Mortensen, 1987, 1992a,b; Machado et al. 1991, 1992). The U-Pb ages define a precise temporal frame of reference and show that intrusion of granitoid magmas and regional metamorphism occurred over a period of 80 Ma during and after the formation of the main volcano-sedimentary assemblages. In addition, the initial Pb isotopic composition of potential end-members has been studied in detail (Gariépy and Allègre, 1985; Brévart et al. 1986; Deloule et al. 1989; Dupré and Arndt, 1990) and will be complemented by new data obtained on the gneiss complexes. Finally, Rive et al. (1990) have provided a comprehensive petrogenetic classification of the plutonic suites, allowing comparisons to be made in time and space over the entire area.

## 2. Geological setting and sampling

The Abitibi and Pontiac Subprovinces are part of the Superior Province of the Canadian Shield (Fig. 1). The Abitibi Subprovince is a typical volcano-plutonic subprovince (Card and Ciesielski, 1986) made of metavolcanic rocks, lesser amounts of metasedimentary rocks and abundant igneous intrusions. Metamorphism is generally below greenschist facies (Jolly, 1978) and recent geological syntheses have been provided by Ludden et al. (1986), Corfu et al. (1989), Rive et al. (1990) and Jackson and Sutcliffe (1990). The Pontiac Subprovince is juxtaposed on the Abitibi Subprovince along the Larder Lake-Cadillac fault (Fig. 1). The Pontiac is covered to the west by Proterozoic sedimentary rocks and truncated to the southeast by the Grenville Front Tectonic Zone (Fig.1). The Pontiac Subprovince includes clastic metasediments containing zircons derived from 2.90 to 2.69 Ga old sources (Gariépy et al., 1984; Davis, 1991). The paragneisses have been intruded by voluminous granitoid plutons between 2.69 and 2.64 Ga (Machado et al. 1991, 1992). The Pontiac Subprovince contains in its southwestern portion mafic volcanic rocks, metasedimentary rocks and tonalite-trondhjemite intrusions. This volcanic belt, erupted between 2.70 and 2.68 Ga (Machado et al. 1992), may represent a klippe of supracrustal materials related to igneous rocks of similar age in the Abitibi Subprovince (Rive et al. 1990).

The tectonic relations between the Pontiac and Abitibi Subprovinces are enigmatic. Supracrustal assemblages in the Abitibi belt are older, having formed between 2.75 Ga and 2.70 Ga (Corfu et al., 1989; Mortensen, 1992a,b), and are generally metamorphosed at a lower grade. For example, the area located northwest of Rouyn-Noranda between the Larder Lake-Cadillac and the Destor-Porcupine breaks (Fig. 1) is dominated by sub-greenschist volcanic rocks of the Blake River Group erupted between 2703 and 2698 Ma (Corfu and Noble, 1992; Mortensen, 1992b). However, the Lacorne tectonic block, a wedge-shaped assemblage of metavolcanic rocks and granitoid plutons located northwest of Val-d'Or (Fig. 1), is anomalous in that it exposes amphibolite facies rocks and 2.65-2.63 Ga muscovite-bearing granites (Kerrich and Feng, 1992), two features that characterize the Pontiac Subprovince. Kerrich and Feng (1992) used these observations to propose that juxtaposition of the Pontiac and Abitibi Subprovinces occurred in a transpressive collisional context which led locally to underthrusting of the Pontiac and concomitant differential uplift of the Abitibi belt. If this is correct, the Lacorne block may be a tectonic window of the Pontiac Subprovince in the Abitibi belt (Kerrich and Feng, 1992).

The tectonic relationships of the Pontiac Subprovince along its southeastern contact with granulite-grade gneisses of the Grenville Front Tectonic Zone (GFTZ) are poorly known. Thermo-barometric measurements (Indares and Martignole, 1989), Rb-Sr studies (Doig, 1977), Pb isotopic signatures of major metamorphic minerals (Gariépy et al., 1990) and U-Pb analyses of zircon (Krogh and Wardle, 1984) and monazite (Philippe et al. 1990) in the gneisses of GFTZ demonstrate that the "Grenvillian" rocks underwent high grade metamorphism in the late Archean between 2.65 to 2.63 Ga. These ages are similar to those of several plutons and gneisses in the Pontiac Subprovince and the Lacorne block, and possibly indicate genetic linkage.

Granitoid rocks are a major constituent of the Pontiac and the central Abitibi Subprovinces. Rive et al. (1990) have divided them into 8 main suites, labeled A to H, on the basis of field relationships, petrological criteria and geochemical data. Note that the aim of the classification is primarily to group intrusions of similar petrogenetic affiliation: it is likely that the intrusion of individual bodies considerably overlap in time. Results will be presented here for those 6 suites which are the most abundant and which cover the entire history of the Subprovinces.

The granitoid rocks of Suite A consist of biotite-bearing dioritic to trondhjemitic orthogneisses. They are closely associated to metasedimentary sequences (Rive et al. 1990). All known massifs of that suite have been sampled. These are (Fig. 1; Table 1): Allemand, Lac des Quinze and Opasatica in the Pontiac Subprovince (#1 to 5; Fig. 1); Bernetz in the Abitibi Subprovince (#9); and one of the gneisses from the Opatica subprovince (#8) which define the northern boundary of the Abitibi Subprovince. U-Pb for the Allemand and Lac des Quinze gneisses yielded minimum ages of 2685 Ma (Machado et al., 1991, 1992) while concordant titanites record a metamorphic overprint occurring at 2637 Ma in the Allemand and 2660 Ma in the Opasatica gneisses. The Bernetz and Opatica gneisses remain undated. Amphibolite facies gneisses were also collected south of the Pontiac Subprovince, in the Grenville Front Tectonic Zone. In this area, the rocks mainly consist of quartzofeldspathic gneisses and migmatites. Mobilisates (#6) and restites (#7) from two localities within 5 km of the Front have been analyzed.

Suite B and C mainly consist of mafic intrusions such as layered complexes, anorthosite and gabbro. Rocks of these two suites have not been sampled because they likely lack any primary K-feldspars.

Suite D consists of large tonalite and granodiorite or trondhjemite plutons (Rive et al. 1990) intruded between 2718 and 2690 Ma (Frarey and Krogh, 1986; Mortensen, 1992b). The suite is syn- to late-volcanic and probably comagmatic with intermediate and felsic volcanic series (Ludden et al., 1986). Three bodies of that suite have been sampled: the Belleterre-Fugerville tonalite (#10-12; Fig. 1), which is associated to the metavolcanic rocks of the southern Pontiac Subprovince, and the Poularis (#13-14) and Taschereau (#15) plutons in the Abitibi Subprovince. The data obtained by Gariépy and Allègre (1985) on the Lac Dufault intrusion (#42), now independently dated at 2690±2 Ma (Mortensen, 1992b), will be used for comparison.

Suites E and F consist of monzodiorite to granodiorite plutons that postdate the volcanic cycles in the Abitibi Subprovince, yielding ages in the range of 2696 to 2669 Ma (Machado et al. 1991, 1992; Mortensen, 1992b). They are distinguished from one another by the presence of clinopyroxene in Suite E (Rive et al. 1990). The samples from plutons of Suites E were collected in both Subprovinces (#16-24; Fig. 1) while plutons of Suite F (#25-28) were sampled in the Pontiac Subprovince only.

Suite G comprises primarily clinopyroxene-bearing monzonites and, in contrast to Suites E and F, occurs as small discrete intrusions lacking any associated granodiorite (Rive et al. 1990). It is also considered to be syn- to late-tectonic and the Lac Simard Nord and the

Lac Fréchette intrusions have yielded similar ages of 2685 Ma (Mortensen et al. 1988; Machado et al. 1992). Three plutons of this suite have been sampled in the Pontiac Subprovince (#29-32) and one in the Abitibi (#33). The rocks of Suites E, F and G are characteristically enriched in alkalis, Ba, Sr and light rare-earth elements, and Rive et al. (1990) suggested that they were derived from mantle sources enriched in large-ion lithophile elements.

Suite H consists of leucocratic intrusives (Rive et al. 1990) and is restricted to the Pontiac Subprovince and the Lacorne block. The interior of the plutons exposes two mica monzogranites while the marginal phases often contain only muscovite. The Décelles batholith is a complex of monzogranitic intrusions and muscovite granites underlying most of the central part of the Pontiac Subprovince (Fig. 1). It is characterized by the presence of recognizable xenoliths of gneisses and metasedimentary rocks, abundant pegmatites and aplites crosscutting each other, and by its heterogeneity at the outcrop scale. The monzogranites have been sampled at five localities (#34-38; Fig. 1) and the granitic dykes at two sites (#39-40). The Hallé (#34) and Garakonthié (#36) localities have yielded U-Pb ages of 2658 and 2651 Ma (Machado et al. 1992). The Lamotte intrusion (#41) which outcrops in the Lacorne block has been dated at 2641 Ma (Machado et al. 1992), the youngest age reported so far for a magmatic rock in the Abitibi Subprovince. Data for the Preissac pluton (#43) will also be used (Gariépy and Allègre 1985). The ages of the Suite H plutons support their classification as being late-tectonic (Rive et al. 1990).

## 3. Analytical techniques

Analyses were done only on K-feldspar (KF), a mineral almost devoid of uranium, in order to obtain the best estimate of the initial Pb isotopic composition. Between 3 and 10 mg of clear KF grains were hand-picked from the diamagnetic fraction of a magnetic separator. The fractions were washed in hot 6N HCl for 12 hours, rinsed with distilled water, dried and powdered. The powder was leached with a diluted solution of HF+HBr for 30 minutes; the supernate and the residue were recovered, dissolved in HF and processed through ion exchange separation (Manhès et al. 1980). The leaching treatments were made to preferentially extract, inasmuch as possible, any labile radiogenic Pb present in the KF structure. In two samples from the Lac Simard Sud pluton, populations of fresh and altered KF grains were processed separately to verify the efficiency of the cleaning treatment. The total Pb blank was smaller than 30 pg and negligible. Pb was analyzed using a VG SECTOR mass spectrometer equiped with a Faraday cage. The raw data are corrected for instrumental mass fractionation using a factor of 0.09% $amu^{-1}$. Replicate analyses of the NBS SRM-981 standard yielded a reproducibility of ±0.05% $amu^{-1}$ (1σ) for sample loads ranging from 10 to 150 ng. All reference growth curves were calculated using 4.55 Ga for the age of the Earth and the Pb isotopic composition of the Canyon Diablo troilite (Tatsumoto et al. 1973).

## 4. Results

The analytical results for KF leachates and residues are listed in Table 1. They will be compared to two compositional domains (*e.g.* Fig. 3) representing the Pb isotopic compositions of the late Archean mantle and of evolved crustal materials present in the southern Superior craton (Gariépy and Allègre, 1985).

The less radiogenic "mantle" domain is defined using the compositions of U-poor sulfides from komatiitic lava flows (Brévart et al. 1986; Dupré and Arndt, 1990) and galena from stratabound volcanogenic massive sulfide deposits (Bugnon et al. 1979; Deloule et al. 1989) within the Abitibi Subprovince. The more radiogenic "crustal" domain is delineated with the compositions of U-poor sulfides from banded iron formations (BIF) occurring in the Pontiac and the Abitibi Subprovinces (Deloule et al. 1989).

The likelihood that reservoirs having strictly these isotopic compositions were involved in the genesis of the intrusives is disputable. For example, some of the granitoids may have been generated in an arc setting, in which case the Pb isotopic composition of the mantle could have been significantly modified by subducted crustal materials. One can also advocate that the BIF have averaged, through seawater exchanges, the Pb isotopic compositions of a variety of sources including older crustal rocks that were not present in the Pontiac and Abitibi Subprovinces (Gariépy and Allègre, 1985). Nevertheless, these domains represent the most extreme Pb isotopic compositions found so far in the Abitibi and are useful frames of reference to compare analytical data sets.

The KF residues yield $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios ranging from 13.3 to 14.1, 14.47 to 14.82 and 33.3 to 34.0, respectively (Table 1). In most cases, the leachates are more radiogenic than their corresponding residues. This indicates that labile radiogenic Pb is present in the KF samples, and that the isotope ratios for any residue can only be taken as the maximum values of the initial isotopic composition (e.g. Housh and Bowring, 1991). For example, Fig. 2 shows in the $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagram the analytical results for leachate-residue pairs from three localities of the Belleterre-Fugerville pluton. The data are correlated along a line having a slope of 0.194±0.002 which corresponds to an age of 2.77±0.07 Ga that is comparable, within errors, to the U-Pb zircon age of the intrusion. The variations of the Pb isotopic composition are thus likely the result of in situ growth of radiogenic Pb from initial isotopic compositions that were very similar in the three samples. Consequently, instead of assuming that the least radiogenic residues record the initial isotopic composition, data arrays which should parallel ca. 2.7 Ga isochron will be defined and variations along the $^{207}Pb/^{204}Pb$ axis will be studied.

Figure 3a shows the results obtained for the gneisses of Suite A. The KF residue from the Bernetz gneiss in the Abitibi Subprovince has the least radiogenic Pb isotopic composition and plots just above the mantle domain. The gneisses from the Pontiac Subprovince display highly variable $^{207}Pb/^{204}Pb$ ratios ranging from 14.54 to 14.82. The Baie des Lys gneiss is the most radiogenic plotting above the crustal domain defined by the BIF (Fig. 3a). The KF from two gneisses of the Opatica Subprovince have Pb isotopic compositions similar to those of the Pontiac gneisses, the mafic sample (8b) yields a less radiogenic composition than the leucocratic one (8a) which plots above the crustal domain (Fig. 3a). K-feldspars from two gneisses and a mobilisate collected south of the Grenville Front also have Pb isotopic compositions comparable to those of the Pontiac gneisses. This indicates, as in the case further east in the GFTZ (Gariépy et al. 1990), that high grade metamorphism in the Front Zone occurred in late Archean time.

Figure 3b shows the Pb isotopic compositions determined for KF of Suite D. Regression of the results obtained on KF leachates and residues from four different plutons in the two Subprovinces yields an age of 2.70±0.12 Ga (MSWD = 3.7). Considering the wide geographical distribution of these tonalitic plutons, the limited scatter along the isochron indicates that Suite D magmas were derived from reservoirs having the same Pb isotopic composition. This composition is only slightly more radiogenic than that of the mantle domain and comparable to that of the Bernetz gneiss in the Abitibi Subprovince.

The results obtained on the clinopyroxene-bearing monzodiorite to granodiorite plutons of Suite E are shown on Fig. 3c where the 2.7 Ga isochron defined above has been drawn for reference. The two plutons from the Abitibi Subprovince and most of the samples from the Pontiac Subprovince plot very close to the reference isochron indicating that these magmas were derived from reservoirs isotopically similar to those of Suite D. There are two exceptions: sample #18 from the Rivière à la Loutre pluton, which has been analyzed in duplicate, and sample #21 from the Tour de Belleterre intrusion plot along a parallel isochron that is displaced towards more radiogenic $^{207}Pb/^{204}Pb$ ratios and which intersects the crustal domain (Fig. 3c). Therefore, source reservoirs for these two Pontiac plutons must have been different from that of the other suite E plutons.

In two samples of the Lac Simard Sud pluton, aliquots of altered milky grains (#16) and of KF coated with hematite (#17) were processed separately from the unaltered clear KF. The results obtained on the leachate of the hematite coated KF were quite radiogenic (Table 1) indicating that growth of radiogenic Pb may occur in hematite inclusions. However, the Pb isotopic compositions obtained on the residues of both altered fractions are comparable to those of the unaltered KF aliquots. This shows that the leaching experiments may efficiently remove labile radiogenic Pb, even in KF grains that appear very altered.

Figure 4a shows the Pb isotopic results obtained on three Suite F plutons of the Pontiac Subprovince. The KF residues from the Lac Delvin intrusion are the least radiogenic, yielding Pb isotopic compositions similar to the least radiogenic plutons of Suites D and E. In contrast, the Lac Rémigny and Lac Maple intrusions have more radiogenic Pb isotopic compositions plotting close to and within the crustal domain (Fig. 4a).

The results obtained on the clinopyroxene-bearing monzonites of Suite G are shown in Fig. 4b. The five KF residues have similar Pb isotopic compositions clustering slightly below the crustal domain. The leachates are more radiogenic but they are, within error, on a 2.7 Ga reference isochron through the compositions of the residues, suggesting that the four intrusions were derived from similar and homogeneous reservoirs. This is unexpected because three of the intrusions are very small (< 3 km in diameter) and are spread over a wide geographical area in both Subprovinces.

Figure 4c presents the results for the Suite H leucocratic monzogranites. The KF leachates and residues from the Lamotte and the Preissac (Gariépy and Allègre, 1985) plutons, in the Lacorne block, plot slightly below the crustal domain and define a data array parallel to a 2.7 Ga isochron. In contrast, the monzogranites, pegmatite and aplite from the Pontiac have higher $^{207}Pb/^{204}Pb$ ratios and plot exclusively in the crustal domain (Fig. 4c).

Figure 5a is a compilation of all Pb isotopic results for residues of K-feldspar from granitoid intrusions in the Abitibi and Pontiac Suprovinces, including data from this study, from Gariépy and Allègre (1985) and from Tilton and Kwon (1990) on the syenitic Otto stock in the Abitibi. The diagram shows two important features. Firstly, the Pb isotopic compositions of the granitoids extend from the mantle to the crustal domains, a spread representing 0.3 units of the $^{207}Pb/^{204}Pb$ ratio. The samples within the mantle domain (Fig. 5) are from the Renault and Opemisca plutons, located near the northeastern boundary of the Abitibi Subprovince (Gariépy and Allègre, 1985). In comparison, the least radiogenic granitoids in the Pontiac and in the south-central Abitibi Subprovinces are more radiogenic (*e.g.* Fig. 3c). Secondly, Pb isotopic composition for the Pontiac granitoids are generally more radiogenic than for the Abitibi rocks. For example, the Pontiac granitoids from Suite H and some of the intrusions from Suites E and F are more radiogenic than any of the granitoids of the Abitibi and have Pb isotopic compositions only comparable to those of gneisses from the Pontiac Subprovince, the Opatica belt and the GFTZ.

The variations of the $^{208}Pb/^{204}Pb$ ratios in the KF residues are shown on Fig. 5b where they are compared to the composition of the least radiogenic sulfides from Abitibi komatiites (mantle domain) and banded iron formations (crustal domain). The sulfides from the banded iron formations have high $^{208}Pb/^{204}Pb$ ratios (Fig. 5b): this reflects the general geochemical behaviour of Th which is more incompatible than Pb leading thus, through time, to a continental crust reservoir having a mean Th/Pb ratio larger than that of the bulk Earth (*e.g.* Allègre et al. 1988). As in Fig. 5a, the KF have $^{208}Pb/^{204}Pb$ isotopic compositions spreading between the two end-members (Fig. 5b). However, the isotopic signatures of the granitoid rocks from the two Subprovinces are not as distinct from each other, albeit almost all KF with very radiogenic $^{208}Pb/^{204}Pb$ ratios appear to be found only in the Pontiac Subprovince.

The $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagram is a less sensitive source discriminator than the $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagram, for two principal reasons. Firstly, the $^{208}Pb/^{204}Pb$ ratio of an Archean K-feldspar is determined with much lower absolute accuracy (typically $\pm 0.13$, $2\sigma$) than the $^{207}Pb/^{204}Pb$ ratio ($\pm 0.04$). Secondly, most KF leachates have $^{208}Pb/^{204}Pb$ ratios that are more radiogenic than their corresponding residue (Table 1) showing that traces of Th are present in K-feldspar (or in mineral inclusions, fluid inclusions, etc.). The average Th/U ratio of K-feldspar, calculated using the results obtained for leachate-residue pairs and assuming a crystallization age of 2.7 Ga, is close to 3. However, any mixture of the mantle and crust end-members shown in Fig. 5b would also plot along a trend corresponding to an apparent Th/U ratio of about 3. Thus, primary variations of the initial $^{208}Pb/^{204}Pb$ ratios are probably obscured by post-crystallization radiogenic growth of $^{208}Pb$ which cannot be totally eliminated by the leaching treatment. This sharply contrasts with the U-Pb systematics where radiogenic growth of $^{206}Pb$ and $^{207}Pb$ displaces the isotopic compositions away from their initial values along parallel isochrons, but almost perpendiculary to the mixing trend.

## 5. Discussion

### *5.1 The Pb reservoirs*

In a study of komatiites, mafic volcanic rocks and associated sulfides from Archean green-stone belts in different shield areas, Dupré and Arndt (1990) attributed inter-cratonic differences in the initial Pb isotopic compositions of the greenstones to the presence or absence, and the age, of underlying granitoid basement. For example, the Kambalda greenstones of the Yilgarn Block, which are underlain by granitoid crust older than 3.0 Ga, are contaminated and do not record the isotopic composition of their mantle sources (Dupré and Arndt, 1990). In contrast, Dupré and Arndt (1990) concluded that the Abitibi greenstones, where older granitoid basement appears absent, were not highly influenced by crustal contamination.

Indeed, as shown on Fig. 5, some of the granitoid intrusions from the Abitibi Subprovince have compositions comparable to those of sulfides associated with mafic volcanic rocks. These granitoid magmas were thus either derived from the mantle or from crustal precursors with a very short residence time in the continental environment. However, the data obtained on the gneisses, which are rocks undoubtedly formed by the transformation of crustal precursors, indicate that reservoirs having Pb-isotopic compositions much more radiogenic than the mantle were present in the continental crust. The compositions of several of these gneisses are comparable to and even more radiogenic than the BIF (Fig. 3a). In fact, they overlap the Pb isotopic compositions of magmatic and sedimentary sulfides from Kambalda. This is true for the Pontiac Subprovince, the Opatica belt and the GFTZ, but remains unproven for the Abitibi Subprovince because the only gneissic unit recognized so far (Bernetz) yielded unradiogenic compositions.

Figure 6 is a time evolution diagram showing the Pb isotopic composition of all granitoids and gneisses from the Abitibi and Pontiac Subprovinces and the GFTZ that have been dated with the U-Pb method to precisions better than ±5 Ma. The $^{207}Pb/^{204}Pb_{I\text{-}G}$ parameter plotted on the Y-axis is the intersection between an isochron (I) fitted through the least radiogenic KF residue of a sample and the geochron (G). The slopes of the secondary isochron and of the geochron were calculated using the U-Pb age of the sample.

The diagram shows that the isotopic compositions of all rocks younger than *ca.* 2.68 Ga can be explained by the recycling of crustal precursors having $^{238}U/^{204}Pb$ ratios ($\mu$) of about 12 (Fig. 6), a value that is not unrealistically high for the continental crust. In contrast, the isotopic composition of the rocks older than 2.68 Ga cannot result from the production of radiogenic $^{207}Pb$ within the crust: a $\mu$ value as high as 140 would be necessary to raise the isotopic composition of the least radiogenic granitoids from the Abitibi towards that of the radiogenic plutons in Suites F, G or H (Fig. 6). Taking into account only the compositional variations present in the Abitibi granitoids and the widest possible range of crystallization ages, $\mu$ values in excess of 30 are still required (Fig. 6). Thus, the steep alignments in the time evolution diagram of Fig. 6 can only represent mixing of juvenile magmas with older crustal precursors.

*5.2 The granitoid suites*

*5.2.1 Suite A gneisses*

Growth of new zircons in the Pontiac gneisses occurred concurrently with the intrusion of several plutons, between 2695 and 2685 Ma (Mortensen 1987; Machado et al. 1992). In addition, the Pontiac gneisses are spatially associated with intrusives having similar Pb isotopic compositions. These include: a) the tonalitic gneiss of Lac des Quinze (#5; Table 1) and the Belleterre-Fugerville tonalite of Suite D (#10 to 12); b) the Opasatica gneisses (#3-4) and the Fréchette monzonite (Suite G; #32); and c) the Baie des Lys gneiss (#1-2) and the Décelles intrusion (Suite H; #34-36). These gneisses and granitoids were likely derived from the same parent rocks.

The gneisses from the GFTZ and the melt pods within them all have very high initial $^{207}Pb/^{204}Pb$ ratios comparable only to those of the Baie des Lys gneiss and the Décelles complex. In addition, the U-Pb monazite ages of Philippe et al. (1990) show that peak granulite facies conditions were reached in the GFTZ between 2.64 and 2.66 Ga, a period which corresponds exactly to the emplacement of the Décelles batholith and to the U-Pb titanite ages obtained on the Pontiac gneisses (Machado et al. 1991). Furthermore, the GFTZ gneisses have initial $^{87}Sr/^{86}Sr$ ratios of 0.7021±0.0002 (Doig, 1977), a value significantly higher than that of mantle derived rocks of late Archean age (Machado et al. 1986). All these observations support the concept that the GFTZ is the deeper crustal equivalent of the Pontiac Subprovince and that some of the rocks in both areas are derived from the same crustal precursors.

The gneisses from the Opatica Subprovince are no different from those of the Pontiac and the GFTZ, but the unradiogenic Bernetz gneiss (#9) in the Abitibi must be the by-product of a crustal reservoir containing a high proportion of juvenile rocks, such as mafic to intermediate volcanics of direct mantle derivation.

*5.2.2 Suite D , E and F granitoids*

The tonalite-trondhjemite plutons of Suite D and the clinopyroxene-bearing monzodiorite-granodiorite bodies of Suite E have Pb isotopic compositions similar to the Bernetz gneiss, plotting slightly above the mantle domain. Considering that Suite D plutons are closely associated with calc-alkaline volcanism, one may contend that Suites D and E magmas were derived from the mantle in the context of a subduction zone between 2.72 and 2.69 Ga. The $^{207}Pb/^{204}Pb$ ratio of this mantle source was higher than that of the mantle source of komatiites from the Abitibi (Brévart et al. 1986; Dupré and Arndt, 1990) indicating either that it was modified by subducted sediments or that the magmas were contaminated upon ascending the crust.

The intrusions of Suite D and E lack any spatial organization that is reminiscent of subduction zones, but this may be due to the tectonic disruption of the terranes. Pb isotopes alone cannot fingerprint the exact tectonic environment in which the magmas originated. In fact, one may argue that the melts were produced by intracrustal melting following tectonic thickening based on the observation that the Bernetz gneiss has initial Pb isotopic compositions identical to the Suites D and E intrusives. However, the uniformity of initial isotopic compositions on a regional scale, their proximity to the mantle domain and the close association of Suite D rocks with volcanic assemblages are best explained by a derivation from a mantle source. It remains that the isotopic composition of the magmas record the presence of subducted sediments or assimilated older crust.

Samples from the Rivière à la Loutre and the Tour de Belleterre plutons, two members of Suite E which outcrop in the Pontiac Subprovince, yield compositions in the crustal domain (Fig. 3c). The Tour de Belleterre pluton is, at 2.67 Ga, the youngest intrusive of this suite. This may indicate that younger plutons assimilated more crustal materials or that these were older and/or more abundant in the Pontiac than in the Abitibi Subprovince.

The Suite F plutons were also derived from diversified source areas: the Lac Delvin pluton has an initial Pb isotopic composition similar to that of Suite D, but the Lac Rémigny and Lac Maple intrusions have typical crustal signatures.

*5.2.3 Suite G granitoids*

This suite of clinopyroxene-bearing monzonite stocks, generally less than 2-3 km in diameter, crosscuts a variety of host rocks in the Pontiac and Abitibi Subprovinces. In spite of their small size, which indicates localized magmatic source areas, the plutons have identical and relatively high initial Pb isotopic compositions (Fig. 4b). Local crustal contamination of the melts, whether derived from the mantle or not, is not expected to yield such homogeneous isotopic compositions. This may indicate that some portions of the deeper crust in the Abitibi and Pontiac Subprovinces are homogeneous at the regional scale and have relatively radiogenic Pb isotopic compositions.

*5.2.4 Suite H granitoids*

The plutons of Suite H postdate all other magmatic events in the area, yielding U-Pb ages of 2.66 to 2.64 Ga. This late plutonism was restricted to the Pontiac and the southernmost Abitibi Subprovince. The suite yields the most radiogenic compositions in both Subprovinces, but the Pontiac monzogranites are clearly more radiogenic having compositions comparable only to that of the gneisses (Fig. 3a and 4c). These late intrusives contain abundant xenoliths of metasedimentary rocks and gneisses and were derived in both Subprovinces from crustal, but compositionally different reservoirs. The radiogenic plutons from Suite E and F in the Pontiac Subprovince were also likely derived from the same reservoir as the Décelles batholith.

*5.3 The age of the crustal reservoirs*

The difference in the Pb isotopic compositions of the Abitibi and Pontiac crustal reservoirs is analogous in magnitude to the difference between the Abitibi and the Kambalda belts which Dupré and Arndt (1990) attributed to variations in the age of the basement rocks.

Figure 7 shows the $^{207}Pb/^{204}Pb_{I\text{-}G}$ values for the granitoids and gneisses and two evolution models (Fig. 7a, b) depicting the growth of radiogenic Pb in potential reservoirs.

The single-stage mantle growth curve has been calculated using the mean composition of the 2.70 Ga old Renault and Opemisca plutons (Mortensen, 1992a), the least radiogenic granitoids found in the Abitibi Subprovince (Gariépy and Allègre, 1985). This mantle growth curve corresponds to a $\mu_1$ value of 7.6, but this figure depends highly on the value chosen for $T_0$, the age of the Earth. For example, using $T_0 = 4.50$ Ga yields a higher $\mu_1$ value of 8.0.

The second stage growth curves of Fig. 7a were calculated using the mean $^{207}Pb/^{204}Pb_{I\text{-}G}$ ratio (14.66) of the Pontiac granitoids having U-Pb ages of *ca.* 2.68 Ga. The curves depict the evolution of crustal reservoirs separated at different points in time from the mantle. The $^{238}U/^{204}Pb$ ratio of the ancient reservoir in the Pontiac Subprovince is unknown but most models of crust-mantle evolution set this value between 9.5 and 13.5 (*e.g.* Stacey and Kramers, 1975; Zartman and Doe, 1981; Albarède and Juteau, 1984; Allègre et al. 1988). Using 14.6 as a maximum value for $\mu_2$, Fig. 7a shows that the crustal reservoir of the Pontiac Subprovince has to be made of rocks older than 3.0 Ga if it was derived from a mantle having Pb-isotopic compositions comparable to the least radiogenic granitoids from the Abitibi Subprovince. Figure 7b shows a second set of growth curves spanning the range of $^{207}Pb/^{204}Pb_{I\text{-}G}$ values observed in the Abitibi granitoids older than 2.68 Ga. If $\mu_2$ was 13.6, then the Abitibi crustal reservoir can be made of rocks younger than 2.9 Ga.

There is additional isotopic evidence for older crustal reservoirs beneath the Pontiac than under the Abitibi Subprovince. In a Lu-Hf study of zircons from the southern Abitibi belt west of our study area, Corfu and Noble (1992) reported that the syn- to late-orogenic plutons (2.69-2.68 Ga) have $\varepsilon$Hf values only slightly lower (4.7-3.6) than the 2730-2700 Ma suites of mantle-derived rocks (5.5±0.5). This suggests only minimal contribution from older crustal components in the Abitibi (Corfu and Noble, 1992). In contrast, Pintson et al. (1991) reported $\varepsilon$Nd values as low as -0.2 in some Suite H plutons from the Pontiac Subprovince. This is much lower than the $\varepsilon$Nd values in the range of 2 to 3 that characterize the Abitibi mantle (Machado et al. 1986; Walker et al. 1988) and Pintson et al. (1991) concluded that these rocks were derived from crustal precursors 300 to 400 Ma older.

*5.4 Crustal recycling and tectonic evolution*

A sharp change in the provenance of the granitoid magmas occurred after 2.68 Ga (Fig. 6), an age that corresponds to the deposition of alluvial-fluvial fault related sediments, the formation of trachytic volcanic rocks (Corfu et al. 1991), the emplacement of lamprophyre dykes (Wyman and Kerrich, 1987; Corfu et al. 1989) and the intrusion of syenitic rocks such as the Otto Stock (Corfu and Noble, 1992). This followed the development of the lava series and the calc-alkaline intrusives, and it defines a sequence of events comparable to that observed at convergent plate margins (Corfu and Noble, 1992).

From 2.72 to 2.68 Ga, the granitoid magmas of Suites D, E and F were mainly derived from juvenile mantle sources and only slightly contaminated by older crustal materials.The notable exceptions all occur in the Pontiac Subprovince, which strengthens the inference that it is underlain by a higher proportion of basement rocks older than 3.0 Ga. During the 40 Ma following 2.68 Ga, the granitoid magmas were exclusively derived from radiogenic intracrustal sources. The intracrustal recycling in the southern Abitibi and the Pontiac Subprovinces occurred concurrently with high-grade metamorphism and anatexis of the rocks in the Grenville Front tectonic zone which are identical in age and composition to the Suite H rocks in the Pontiac.

Kerrich and Feng (1992) proposed the following tectonic model, with some features analogous to the Himalaya-Tibet collision zone, to explain the tectonic and metallogenic features present at the boundary between Abitibi and Pontiac Subprovinces. Prior to 2.68 Ga, the Pontiac microcontinent would have been separated from the southern Abitibi belt by oceanic lithosphere. Ocean floor subduction beneath the Abitibi yielded calc-alkaline magmatic activity along its southern margin. Alkaline magmas formed in response to strike-slip motions induced by oblique collision. After collision, the Pontiac microcontinent was locally thrust under the Abitibi and concomitant crustal thickening allowed metasediments to undergo anatexis. Differential uplift exposed part the Pontiac plate as the Lacorne tectonic window that comprises the Preissac and Lamotte plutons of Suite H.

The model of Kerrich and Feng (1992) is consistent with many geologic features recognized at the boundary between the Subprovinces. However, the Pb isotopic results presented here suggest that the Suite H rocks in the Lacorne block were derived from crustal sources different from those in the Pontiac. Extending this plate tectonic model to the rest of the Pontiac Subprovince demands explanations for the huge intracrustal melting events between 2.68 and 2.65 Ga requiring a significant crustal thickening event and the high-grade metamorphism in the GFTZ between 2.65-2.63 Ga.

One possibility is that large sectors of the Pontiac Subprovince were once covered by allochtonous sequences of Abitibi rocks, the remnants of which may be exposed as a klippe of metavolcanic and metasedimentary rocks in the southern area (Rive et al. 1990). Another possibility, yet totally speculative, could invoke northwards thrusting of rocks located south of the Pontiac microcontinent inducing burial of the Pontiac and the GFTZ or else, collision of an additional microcontinent south of the Front zone.

## 6. Conclusions

The Pb isotopic composition of granitoid intrusives from different petrogenetic suites of the Pontiac and Abitibi Subprovinces, when combined with their precise U-Pb crystallization ages, is a useful tool to unravel the magmatic and tectonic histories of the Subprovinces. This study has shown that the earlier intrusives, formed between 2.72 and 2.68 Ga, were principally derived from juvenile mantle sources. A marked change in the source areas of the melts occurred *ca.* 2.68 Ga and, for the following 40 Ma, intracrustal melting of thickened crustal lithosphere predominated. The Pontiac Subprovince is underlain by basement complexes significantly older than the Abitibi, an observation that supports the concept that the Abitibi and Pontiac Subprovinces formed as discrete crustal segments now tectonically juxtaposed on one another. Finally, the Grenville Front tectonic zone was metamorphosed and partially melted in the late Archean and is probably the deep crustal equivalent of the Pontiac Subprovince.

**Acknowledgements**

The authors are grateful to the financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC), the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (FCAR) of Quebec and the Ministère de l'Energie et des Ressources of Quebec. GEOTOP are partly supported by infrastructure grants from NSERC and FCAR. We are also thankful to J.K. Mortensen for providing preprints of his manuscripts, to A. Simard for his support. LITHOPROBE Contribution No. 413.

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**Figure captions**

Fig. 1. Geological map of the Pontiac and central Abitibi Subprovinces modified from Rive et al. (1990). The sampling sites are sequentially numbered and refer to results listed in Table 1.

Fig. 2. $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagram showing the data obtained for three samples of K-feldspar residues (filled symbols) and K-feldspar leachates (open symbols) from the Belleterre-Fugerville intrusion. Error bars in the $^{207}Pb/^{204}Pb$ coordinate are shown at the 95% level of confidence while they are smaller than symbol sizes along the $^{206}Pb/^{204}Pb$ axis. The reference growth curves were calculated using 4.55 Ga for the age of the Earth and the initial composition of the Canyon Diablo troilite; $\mu = ^{238}U/^{204}Pb$.

Fig. 3. $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagrams showing the results obtained on K-feldspar residues (filled symbols) and leachates (open symbols) from Suite A gneisses (a), Suite D tonalite-trondhjemite plutons (b) and Suite E clinopyroxene-bearing monzodiorites to granodiorites (c). The secondary isochron shown in Fig. 3b is a regression through all residues and leachates from Suite D; it is also shown for reference in Fig. 3c. Data sources for Suite D include the results of Gariépy and Allègre (1985) for the Lac Dufault pluton (#42; Fig. 1). Growth curves as in Fig. 2.

Fig. 4. $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagrams showing the results obtained for Suite F monzodiorite to granodiorite plutons (a), Suite G clinopyroxene-bearing monzonite stocks (b) and Suite H two mica monzogranites (c). Data sources for Suite H include the results of Gariépy and Allègre (1985) for the Preissac pluton (#43; Fig. 1). Symbols and growth curves as in Fig. 3.

Fig. 5. a) $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ and b) $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagrams showing the Pb isotopic results obtained on K-feldspar residues from granitoid intrusives of the Abitibi and Pontiac Subprovinces. Data sources include Gariépy and Allègre (1985), Tilton and Kwon (1990) and this study. The open squares with a diagonal in Fig. 5b show the Pb

isotopic compositions of the least radiogenic sulfides associated to Abitibi komatiites (Brévart et al. 1986; Dupré and Arndt, 1990) while the crossed squares show the compositions of the least radiogenic sulfides from Abitibi banded iron formations (Deloule et al. 1989).

Fig. 6. Diagram showing the $^{207}Pb/^{204}Pb_{I-G}$ ratios of gneisses from the GFTZ and the Pontiac, and of granitoids from the Pontiac and Abitibi Subprovinces as a function of their U-Pb crystallization ages. The $^{207}Pb/^{204}Pb_{I-G}$ ratio of each individual sample is defined by the intersection of the geochron with the secondary isochron fitted through the data obtained on a K-feldspar residue. Data sources include Gariépy and Allègre (1985), Frarey and Krogh (1986), Mortensen (1987, 1992a,b), Gariépy et al. (1990), Philippe et al. (1990), Tilton and Kwon (1990), Machado et al. (1991, 1992) and Corfu and Noble (1992). M = mantle; C = crust.

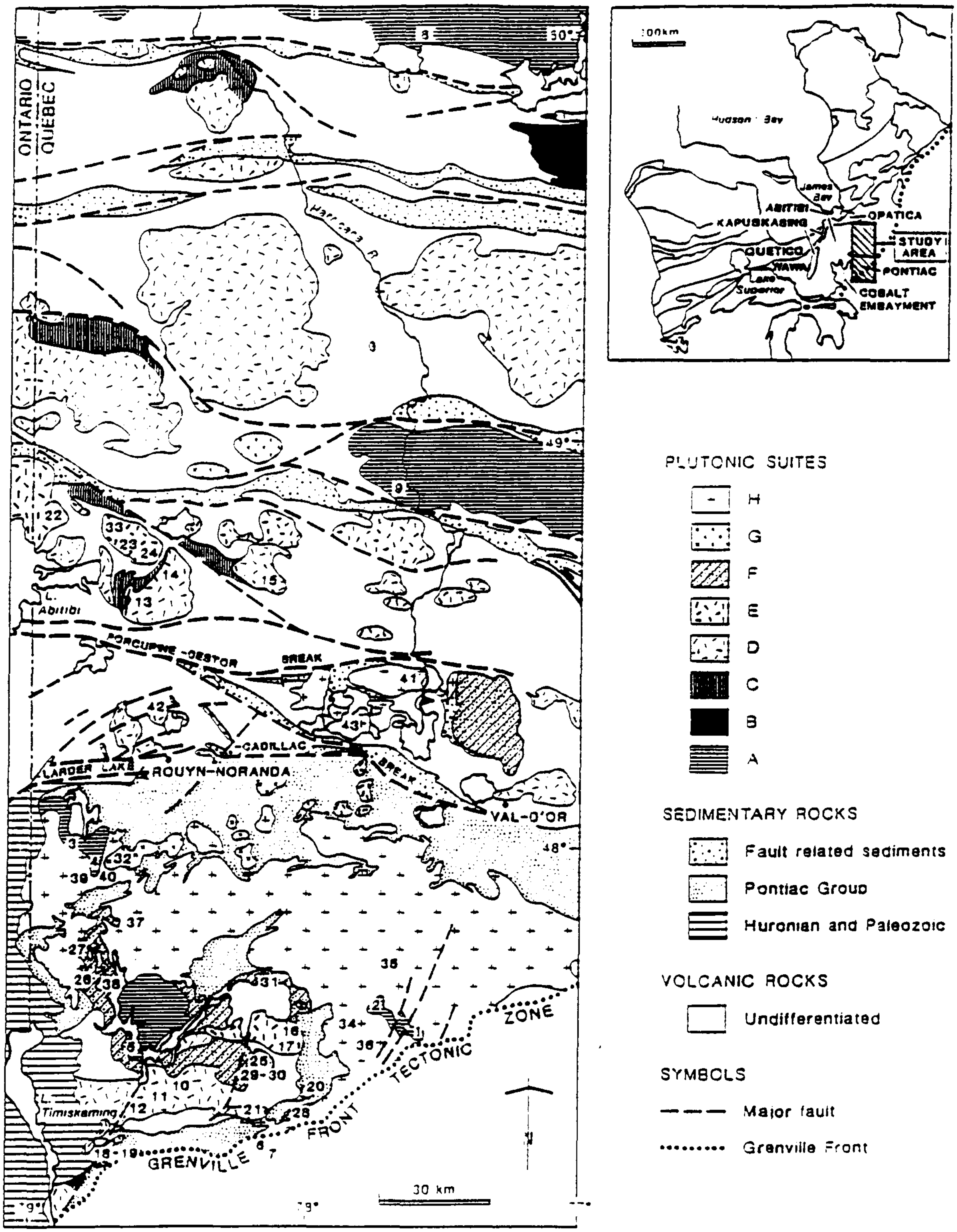
Fig. 7. Plot of $^{207}Pb/^{204}Pb_{I-G}$ vs. time showing, from 3.0 Ga onwards, the evolution of potential reservoirs involved in the genesis of a) the Pontiac and b) the Abitibi granitoid intrusive. The mantle curve ($\mu_1$) depicts the single-stage growth from 4.55 Ga to 2.7 Ga and the tick marks are at 20 Ma intervals. Crustal reservoirs extracted from the mantle will require, as a function of time, $^{238}U/^{204}Pb$ ratios indicated as $\mu_2$ to match the isotopic composition of the most radiogenic granitoid intrusives in each province. See text for choice of end-member parameters. Symbols as in Fig. 6.

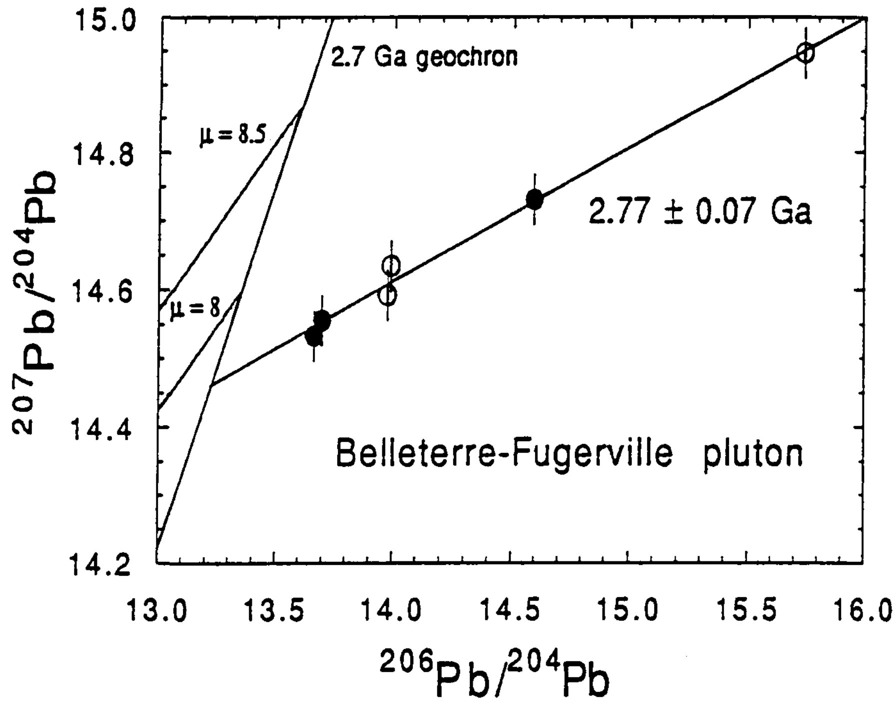
TABLE I. Pb isotopic results

| Suite | Locality | Area | Sample | 206Pb/204Pb | 207Pb/204Pb | 208Pb/204Pb | Age (Ma) |
|---|---|---|---|---|---|---|---|
| A | Baie des Lys | PT | 1 L | 13.724 | 14.654 | 33.430 | |
| | | | 1 R | 13.708 | 14.734 | 33.642 | |
| | | | 2 L | 14.153 | 14.736 | 33.495 | |
| | | | 2 R | 14.146 | 14.824 | 33.735 | |
| A | Opasatica | PT | 3 L | 13.481 | 14.553 | 33.282 | |
| | | | 3 R | 13.440 | 14.551 | 33.269 | |
| | | | 4 L | 13.881 | 14.658 | 33.592 | |
| | | | 4 R | 13.666 | 14.635 | 33.493 | |
| A | Lac des Quinze | PT | 5 L | 14.267 | 14.693 | 33.949 | 2685±9 [1] |
| | | | 5 R | 13.572 | 14.543 | 33.328 | 2695±1 [2] |
| A | GFTZ | | 6 L | 13.789 | 14.725 | 33.579 | |
| | | | 6 R | 13.669 | 14.656 | 33.357 | |
| | | | 7a L | 13.909 | 14.652 | 33.610 | |
| | mafic facies | | 7a R | 13.572 | 14.592 | 33.389 | |
| | | | 7b L | 14.248 | 14.772 | 33.135 | |
| | felsic facies | | 7b R | 14.112 | 14.771 | 33.877 | |
| A | Opatica | | 8a L | 13.595 | 14.631 | 33.456 | |
| | mafic facies | | 8a R | 13.520 | 14.582 | 33.309 | |
| | | | 8b L | 13.861 | 14.740 | 33.947 | |
| | felsic facies | | 8b R | 13.746 | 14.774 | 33.893 | |
| A | Bernetz | AB | 9 L | 13.382 | 14.543 | 33.355 | |
| | | | 9 R | 13.338 | 14.487 | 33.218 | |
| D | Belleterre-Fugerville | PT | 10 L | 13.993 | 14.634 | 33.761 | 2705±3 [1] |
| | | | 10 R | 13.697 | 14.555 | 33.357 | |
| | | | 11 L | 15.742 | 14.947 | 34.641 | |
| | | | 11 R | 14.594 | 14.731 | 33.513 | |
| | | | 12 L | 13.979 | 14.592 | 33.805 | |
| | | | 12 R | 13.662 | 14.533 | 33.359 | |
| D | Poularis | AB | 13 L | 13.647 | 14.581 | 33.465 | |
| | | | 13 R | 13.376 | 14.496 | 33.244 | |
| | | | 14 L | 13.448 | 14.528 | 33.343 | |
| | | | 14 R | 13.399 | 14.537 | 33.368 | |
| D | Taschereau | AB | 15 L | 13.945 | 14.635 | 33.679 | 2718±2 [3] |
| | | | 15 R | 13.557 | 14.516 | 33.337 | |
| E | Lac Simard Sud | AB | 16 M L | 13.605 | 14.521 | 33.301 | |
| | | | 16 M R | 13.441 | 14.512 | 33.208 | |
| | | | 16 L | 13.401 | 14.506 | 33.186 | |
| | | | 16 R | 13.397 | 14.518 | 33.218 | |
| | | | 17 C L | 14.505 | 14.691 | 34.056 | |
| | | | 17 C R | 13.399 | 14.526 | 33.213 | |
| | | | 17 L | 13.386 | 14.506 | 33.162 | |
| | | | 17 R | 13.452 | 14.562 | 33.359 | |
| E | Rivière à la Loutre | PT | 18 L | 15.061 | 14.931 | 33.813 | |
| | | | 18 R | 14.645 | 14.881 | 33.673 | |
| | | | 18 R | 14.618 | 14.891 | 33.719 | |

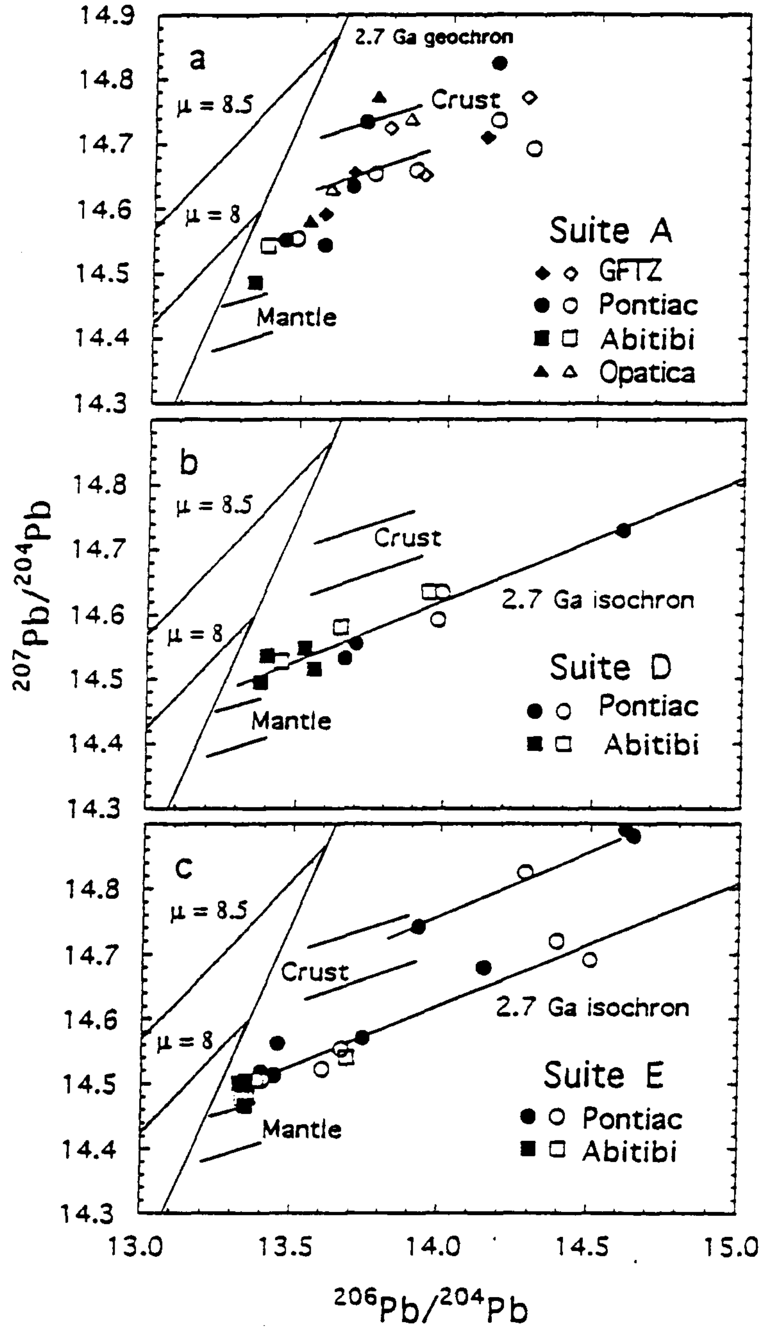
| Suite | Locality | Area | Sample | 206Pb/204Pb | 207Pb/204Pb | 208Pb/204Pb | Age (Ma) |
|---|---|---|---|---|---|---|---|
| E | Rivière à la Loutre | PT | 19 L | 14.388 | 14.720 | 34.482 | |
| | | | 19 R | 14.147 | 14.679 | 34.601 | |
| E | Lac Soufflot | PT | 20 L | 13.669 | 14.553 | 33.403 | |
| | | | 20 R | 13.739 | 14.571 | 33.373 | |
| E | Tour de Belleterre | PT | 21 L | 14.279 | 14.825 | 33.692 | 2669±3 [4] |
| | | | 21 R | 13.925 | 14.742 | 33.523 | |
| E | Lac Abitibi | AB | 22 L | 13.335 | 14.477 | 33.255 | 2690±1 [5] |
| | | | 22 R | 13.345 | 14.504 | 33.293 | |
| E | Colombourg | AB | 23 L | 13.686 | 14.540 | 33.410 | 2696±3 [5] |
| | | | 23 R | 13.345 | 14.466 | 33.148 | |
| | | | 24 L | 13.352 | 14.479 | 33.267 | |
| | | | 24 R | 13.324 | 14.501 | 33.308 | |
| F | Lac Delvin | PT | 25 L | 13.919 | 14.581 | 33.311 | |
| | | | 25 R | 13.481 | 14.517 | 33.242 | |
| F | Lac Rémigny | PT | 26 L | 13.531 | 14.586 | 33.366 | 2684±3 [1] |
| | | | 26 R | 13.528 | 14.626 | 33.388 | |
| | | | 27 L | 13.547 | 14.606 | 33.351 | |
| | | | 27 R | 13.501 | 14.593 | 33.513 | |
| F | Lac Maple | PT | 28 L | 13.818 | 14.629 | 33.342 | 2678±3 [4] |
| | | | 28 R | 13.699 | 14.731 | 33.633 | |
| G | Guillet Nord | PT | 29 L | 13.595 | 14.619 | 33.325 | |
| | | | 29 R | 13.569 | 14.594 | 33.275 | |
| | | | 30 L | 13.654 | 14.639 | 33.491 | |
| | | | 30 R | 13.626 | 14.609 | 33.407 | |
| G | Lac Simard Nord | PT | 31 L | 13.795 | 14.648 | 33.512 | 2686±4 [4] |
| | | | 31 R | 13.469 | 14.569 | 33.346 | |
| G | Lac Fréchette | PT | 32 L | 14.387 | 14.789 | 34.067 | 2685±8 [2] |
| | | | 32 R | 13.444 | 14.563 | 33.253 | |
| G | LaSarre | AB | 33 R | 13.464 | 14.574 | 33.289 | |
| H | Hallé | PT | 34 L | 14.072 | 14.777 | 34.046 | 2651±2 [1] |
| | | | 34 R | 13.679 | 14.676 | 33.717 | |
| H | Rapides 7 | PT | 35 L | 14.228 | 14.782 | 34.143 | |
| | | | 35 R | 13.549 | 14.628 | 33.433 | |
| H | Garakonthié | PT | 36 L | 15.062 | 14.944 | 34.497 | 2658±2 [1] |
| | | | 36 R | 14.019 | 14.768 | 33.408 | |
| H | Beaumesnil | PT | 37 L | 13.973 | 14.754 | 33.963 | |
| | | | 37 R | 13.700 | 14.694 | 33.525 | |
| H | Roulier | PT | 38 L | 14.156 | 14.719 | 33.605 | |
| | | | 38 R | 13.723 | 14.657 | 33.463 | |
| H | Pegmatite | PT | 39 L | 14.547 | 14.859 | 33.605 | |
| | | | 39 R | 13.921 | 14.710 | 33.362 | |
| H | Aplite | PT | 40 L | 14.195 | 14.765 | 33.585 | |
| | | | 40 R | 13.728 | 14.681 | 33.430 | |
| H | Lamotte | AB | 41 L | 14.581 | 14.789 | 33.812 | 2641±2 [1] |
| | | | 41R | 13.765 | 14.673 | 33.525 | |

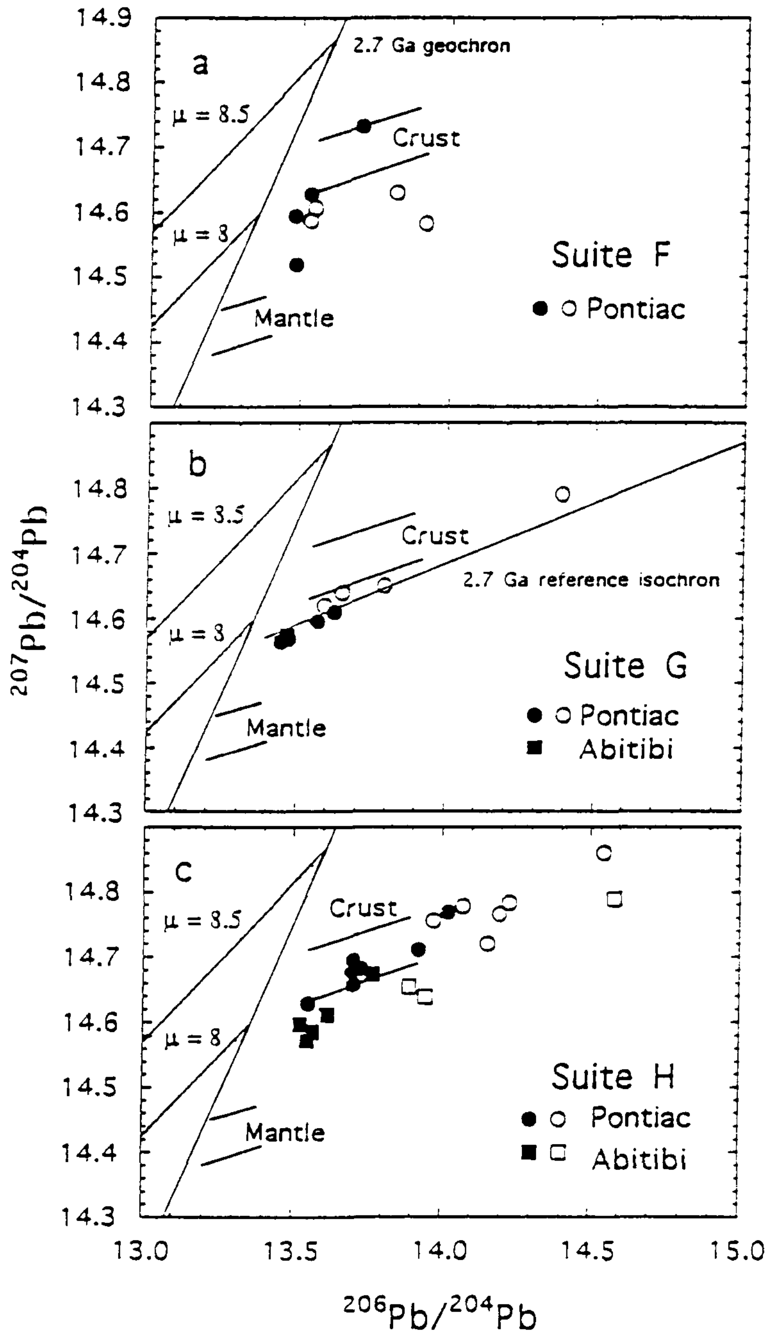
AB: Abitibi. PT: Pontiac. L: Leachate. R: Residue. M: Milky. C: Hematite coated. [1] Machado et al. (1992). [2] Mortensen et al. (1988). [3] Frarey and Krogh (1986). [4] Machado et al. (1991). [5] Mortensen (1992b)


ONTARIO
QUEBEC
50°
49°
48°
Harricana R.
L. Abitibi
PORCUPINE - DESTOR BREAK
CADILLAC BREAK
LARDER LAKE
ROUYN-NORANDA
VAL-D'OR
Timiskaming
GRENVILLE FRONT TECTONIC ZONE
30 km
79°
Hudson Bay
James Bay
ABITIBI
KAPUSKASING
OPATICA
QUETICO
WAWA
STUDY AREA
PONTIAC
Lake Superior
COBALT EMBAYMENT
PLUTONIC SUITES
H
G
F
E
D
C
B
A
SEDIMENTARY ROCKS
Fault related sediments
Pontiac Group
Huronian and Paleozoic
VOLCANIC ROCKS
Undifferentiated
SYMBOLS
Major fault
Grenville Front

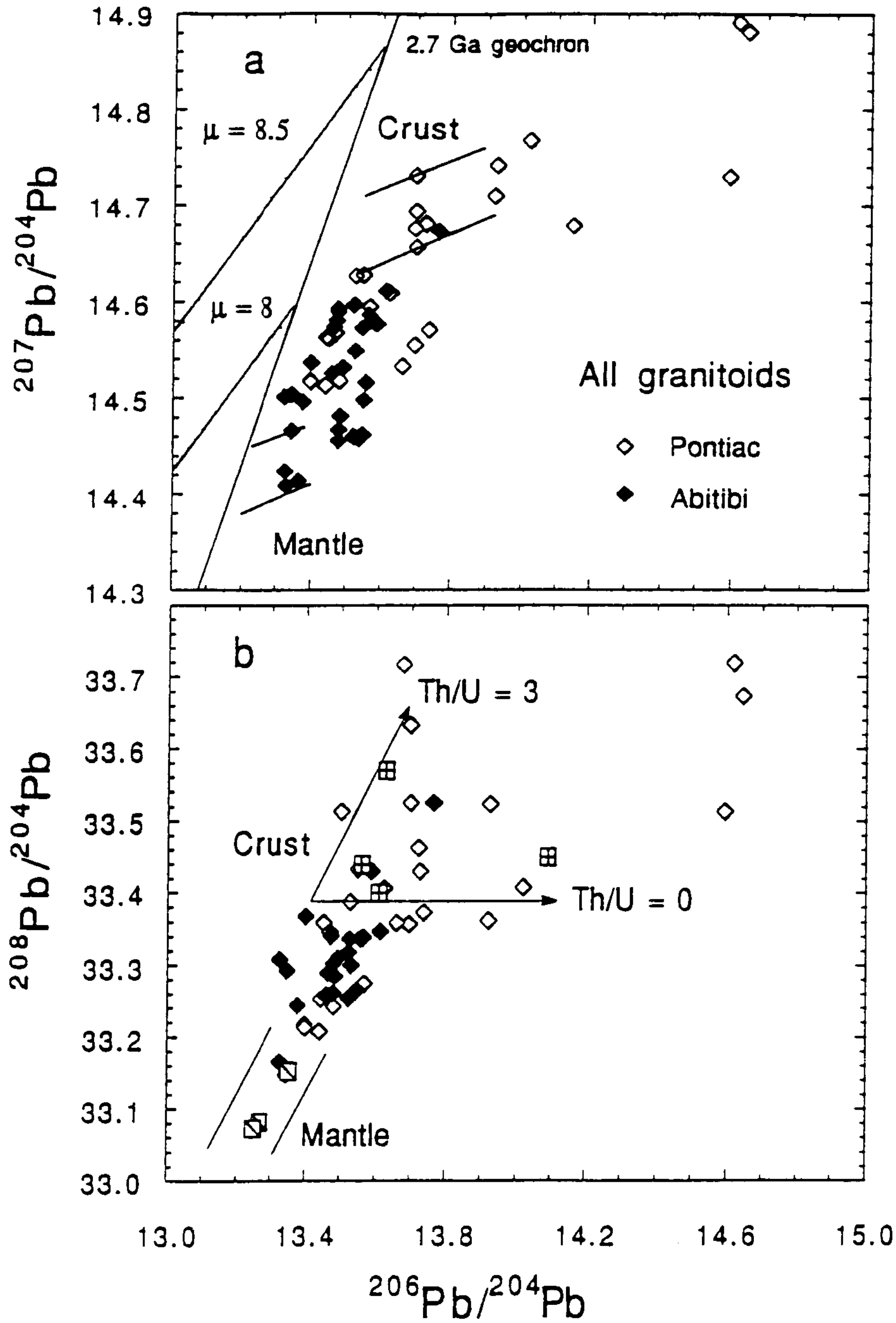


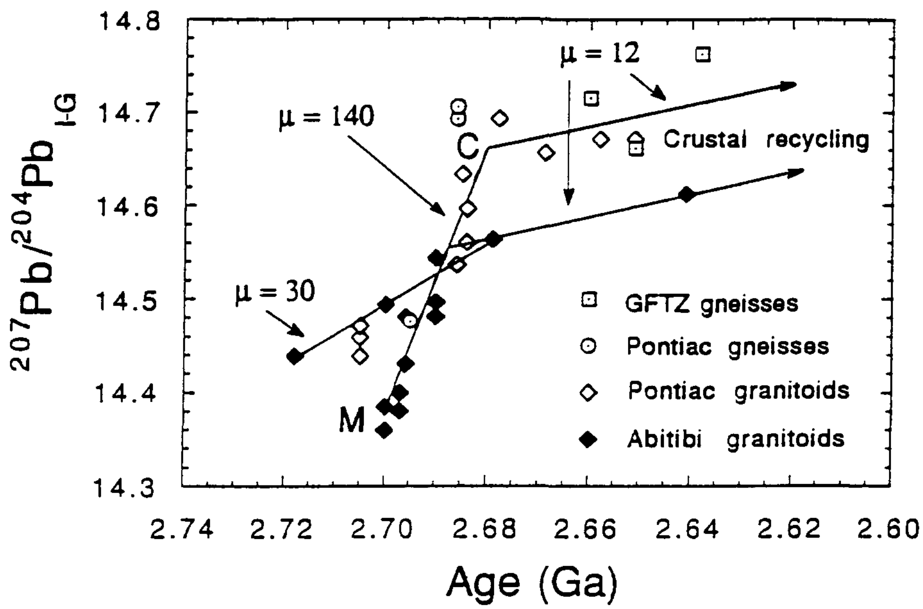
2.7 Ga geochron
μ = 8.5
μ = 8
2.77 ± 0.07 Ga
Belleterre-Fugerville pluton
15.0
14.8
14.6
14.4
14.2
13.0
13.5
14.0
14.5
15.0
15.5
16.0
207Pb/204Pb
206Pb/204Pb


a
2.7 Ga geochron
μ = 8.5
μ = 8
Crust
Mantle
Suite A
GFTZ
Pontiac
Abitibi
Opatica
b
μ = 8.5
μ = 8
Crust
2.7 Ga isochron
Mantle
Suite D
Pontiac
Abitibi
c
μ = 8.5
μ = 8
Crust
2.7 Ga isochron
Mantle
Suite E
Pontiac
Abitibi
14.9
14.8
14.7
14.6
14.5
14.4
14.3
13.0
13.5
14.0
14.5
15.0
$^{207}Pb/^{204}Pb$
$^{206}Pb/^{204}Pb$

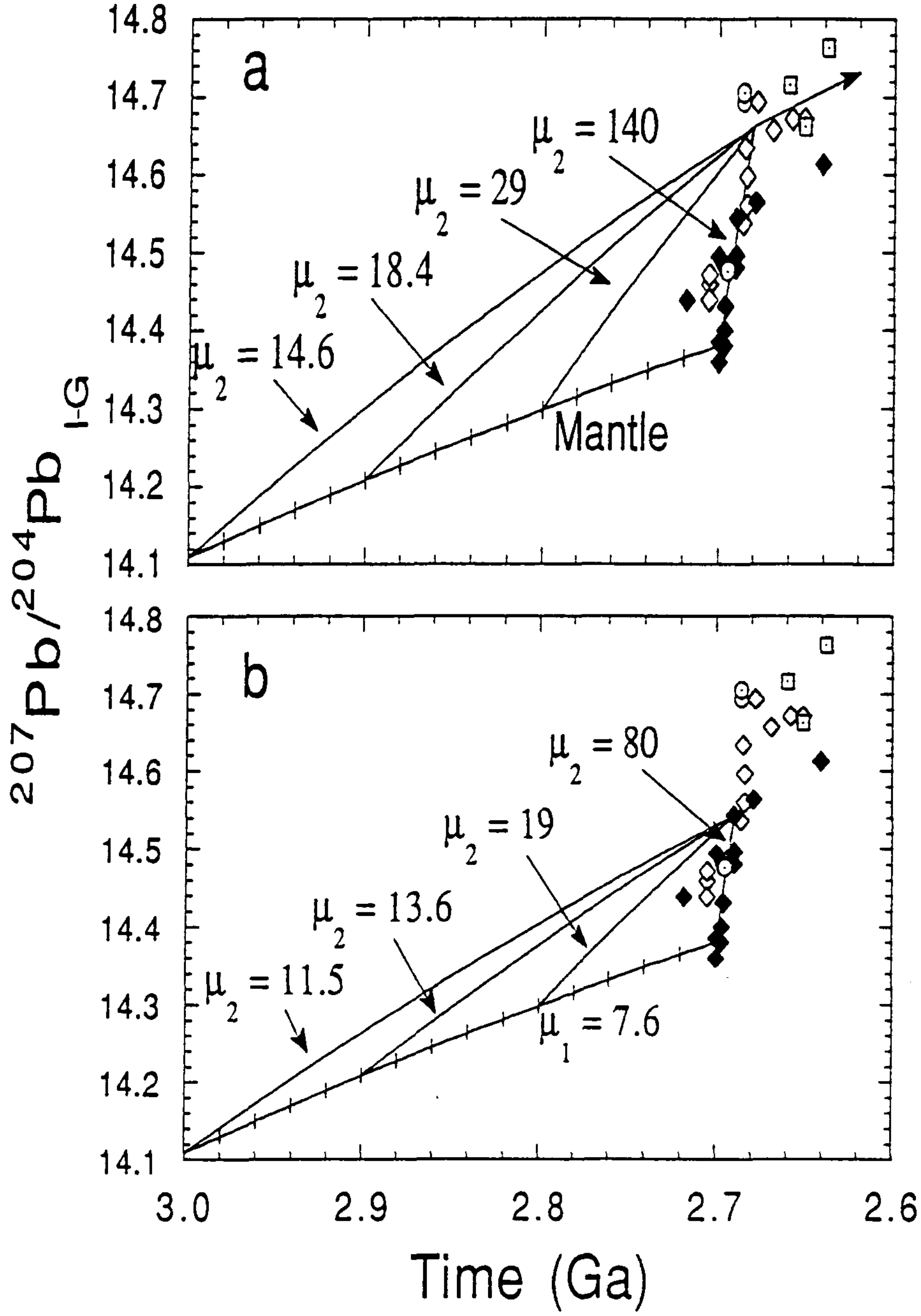


14.9
14.8
14.7
14.6
14.5
14.4
14.3
a
2.7 Ga geochron
μ = 8.5
μ = 8
Crust
Mantle
Suite F
● ○ Pontiac
b
Crust
2.7 Ga reference isochron
Suite G
● ○ Pontiac
■ Abitibi
c
Suite H
● ○ Pontiac
■ □ Abitibi
13.0
13.5
14.0
14.5
15.0
$^{207}Pb/^{204}Pb$
$^{206}Pb/^{204}Pb$


14.9
14.8
14.7
14.6
14.5
14.4
14.3
$^{207}Pb/^{204}Pb$
a
2.7 Ga geochron
$\mu = 8.5$
$\mu = 8$
Crust
Mantle
All granitoids
Pontiac
Abitibi
33.7
33.6
33.5
33.4
33.3
33.2
33.1
33.0
$^{208}Pb/^{204}Pb$
b
Th/U = 3
Th/U = 0
Crust
Mantle
13.0
13.4
13.8
14.2
14.6
15.0
$^{206}Pb/^{204}Pb$



$^{207}Pb/^{204}Pb_{I-G}$
14.8
14.7
14.6
14.5
14.4
14.3
2.74
2.72
2.70
2.68
2.66
2.64
2.62
2.60
Age (Ga)
μ = 12
μ = 140
μ = 30
C
M
Crustal recycling
GFTZ gneisses
Pontiac gneisses
Pontiac granitoids
Abitibi granitoids


a
$\mu_2 = 140$
$\mu_2 = 29$
$\mu_2 = 18.4$
$\mu_2 = 14.6$
Mantle
b
$\mu_2 = 80$
$\mu_2 = 19$
$\mu_2 = 13.6$
$\mu_2 = 11.5$
$\mu_1 = 7.6$
$^{207}Pb/^{204}Pb_{I-G}$
Time (Ga)
14.8
14.7
14.6
14.5
14.4
14.3
14.2
14.1
3.0
2.9
2.8
2.7
2.6

# Pb isotope geochemistry of molybdenite ores from the Grenville and Superior Provinces, Canadian Shield: geochronological potential

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## Abstract

Six molybdenite occurrences from the Canadian Shield have been sampled for Pb isotopic analyses. These are the Massbéryl Corporation property in the late Archean Abitibi greenstone belt which consists of a pegmatitic dyke bearing molybdenite and spodumene; the Pidgeon Molybdenum Mines in the Wabigoon greenstone belt of the Superior Province consisting of a stockwork of molybdenite developed in sediments at the contact of a granite; a molybdenite bearing pegmatite near Baie-Ste-Catherine in the Baie Comeau segment of the Grenville Province; and three localities within the Central Metasedimentary belt of the southern Grenville: the Moss mine in the Onslow syenite, the skarn deposit of the Hunt mine and the Joiner deposit formed in pegmatites croscutting paragneisses.

Our results show that internally consistent Pb-Pb isochrons can be defined for molybdenite using a differential dissolution technique provided that a pure mineral separate is used. The closure temperature of diffusion for the U-Pb system in molybdenite appears to be low and comparable to that of the K-Ar system in muscovite i.e. 350-400°C. Thus molybdenite can be thermally reset, as has occurred at 2.1 Ga for the Pidgeon deposit in the Wabigoon subprovince. This age coincides with the intrusion of the Fort Frances dyke swarm. Thermal resetting of molybdenite appears to induce a larger loss of uranium relative to Pb and Th. The Th/U ratio of molybdenite is systematically lower than 2.0 which probably indicates that the solid-liquid partition coefficient of Th in molybdenite is much lower than that of U. In addition, it is possible that molybdenite from late-stage magmatic deposits like pegmatites or skarns is characterized by very high $^{238}U/^{204}Pb$ ratios (30-230) and very low Th/U ratios (0.7-1.2) which may reflect the greater involvement of a meteoric water source. Finally, in all the studied deposits molybdenite was derived from source reservoirs having relatively high time-integrated $^{238}U/^{204}Pb$ ratios.

## Introduction

Direct and precise dating of sulfide minerals could become a very helpful tool to unravel the metallogenesis of a variety of ore deposits. Dating of ore deposition is most frequently done by K-Ar or Ar-Ar on secondary hydrated silicates that develop when intense alteration is associated with ore precipitation. Galena Pb model ages have been widely used in base metal deposits, but are not a precise geochronological tool because of the uncertainties concerning the model growth curves and controversy surrounding the origin of the deposits (Gulson 1986).

Traces of uranium in cogenetic lead-poor minerals should allow the *in situ* growth of radiogenic Pb that can be used for dating purposes. Unfortunately, the U-Pb system is frequently perturbed in sulfide minerals due to loss and/or gain of U and Pb. In comparison, there are some successful examples of mineralizations which have yielded $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ isochron ages that approximate the true age of crystallization (determined independently). These include Ni-Cu mineralization in southern Finland (Häkli et al. 1975; Papunen 1980), sulfides from the volcanogenic Kidd Creek deposit in Ontario (Bugnon et al. 1979), Ni-Fe associated with Archean komatiites (Brévart et al. 1986; Dupré and Arndt 1990) and Fe-Ni-Cu-Zn-Mo sulfides from a variety of occurences in the Abitibi belt (Deloule et al. 1989). This suggests that there are cases where the U-Pb decay scheme in sulfides remained a closed system or was perturbed only very recently.

Despite their good agreement with the known age of crystallization, Pb-Pb sulfide isochrons cannot be considered as "precise". Typically, Archean sulfide isochrons have errors of 40 to 100 Ma. In some cases this may be due to an open system behavior, but in others this is because the dispersion of the analytical results in the isochron diagram is not sufficiently large.

In order to maximize the spread of the Pb ratios in the isochron diagram, Deloule et al. (1989) devised some acid leaching experiments of the sulfide minerals. The experiments are based on the concept that the radiogenic Pb component that developed in the mineral through U decay is located in crystal regions that have suffered radiation damages. The radiogenic Pb in these regions might thus be dissolved preferentially to the initial common Pb incorporated in the crystal lattice. Deloule et al. (1989) showed that mild acid leaching of a variety of sulfides removes a Pb component that is more radiogenic than that in the residual mineral. The most efficient experiment was done on a late Archean molybdenite which yielded leachates with $^{206}Pb/^{204}Pb$ ratios greater than 50 (Deloule et al. 1989). Whether this is due to the structure of molybdenite which allows efficient dissolution of the radiogenic Pb or to an initial U content higher than most base metal sulfides, or a combination of both, is not known.

The purpose of this study was to develop further the leaching technique and evaluate its geochronological potential using Pb isotopic results obtained on molybdenite. Results will be presented for six Precambrian molybdenum deposits hosted in pegmatites, granites and skarns of the Superior and Grenville Provinces.

## Geological outline and sampling

Figure 1 shows the location of the six studied deposits. Sample MB is from a prospect of the Massberyl Corporation in the southeastern part of the late Archean Abitibi Subprovince of the Canadian Shield (Fig. 1). The sample was taken from a K-feldspar-muscovite-garnet-spodumene dyke bearing cm-size grains of molybdenite and beryl. The dyke is located at the periphery of the Lacorne intrusion and is one of several Mo deposits associated with this pluton and with the nearby Lamotte and Preissac granitoid intrusions.

The Lacorne pluton comprises hornblende-biotite gabbro breccia to monzonite and biotite-hornblende diorite to granodiorite. It is not dated, but other Abitibi plutons of similar lithology have yielded ages of 2.68 to 2.69 Ga (Machado et al. 1991, 1992). However, the molybdenite bearing dyke is associated with a muscovite-biotite-garnet leucomonzogranite (Bourne and Danis 1987). Two-mica granites in the Abitibi and the Pontiac Subprovinces are systematically younger than all other intrusions, yielding ages in the range of 2.66 to 2.64 Ga (Machado et al. 1991, 1992). Feng and Kerrich (1992) reported zircon Pb evaporation ages of 2631±20 and 2643±12 Ma for garnet-muscovite bearing granites of the Lacorne pluton.

However, muscovite from the Lacorne pegmatites records younger $^{40}Ar/^{39}Ar$ ages of 2.59-2.61 Ga interpreted to reflect cooling below the 350°C isotherm (Feng et al. 1992).

Samples PM1 and PM2 are from the property of the Pidgeon Molybdenum Mines in the Wabigoon Subprovince of the Superior Province (Fig. 1). The property is located about 60 km to the southwest of Sioux Lookout (Fig. 1) and the geology of the area has been described by Turner and Walker (1973) and Trowell et al. (1980). The deposit consists of quartz and pegmatitic veins forming a stockwork along the east margin of the contact between the Lateral Lake granite and surrounding sedimentary units (Johnson 1968). Molybdenite is present as scattered to abundant flakes in granite pegmatites (samples PM1 and PM2), aplite stringers, and pegmatitic quartz vein crosscutting a granodiorite.

The main magmatic activity in the Wabigoon Subprovince occurred between 2.74 and 2.73 Ga as indicated by the U-Pb ages of plutonic and volcanic rocks from the Sturgeon, Sioux Lookout and Eagle-Wabigoon Lake areas (Davis and Trowell 1982; Davis et al. 1982). Late volcanic activity has been reported in the Sturgeon Lake and the Kakagi Lake areas where tuffs yield U-Pb ages between 2720 and 2710 Ma (Davis and Trowell 1982; Davis and Edwards 1982).

Samples BSC and BSCG were collected in the Central Zone (Rivers et al. 1989) of the Grenville Province, an area exposing gneisses and monzonite, granite, and anorthosite intrusions (Rondot 1972; Miller 1973; Frith and Doig 1973). The sample was taken from an undeformed quartz-feldspar-biotite pegmatite containing disseminated molybdenite. The pegmatite is located at Baie Sainte-Catherine, near the mouth of the Saguenay River, where it intrudes paragneisses. Whole-rock Rb-Sr studies indicate metamorphic ages ranging from 1.5 to 1.3 Ga for the paragneisses and between 1.1 and 1.0 Ga for the monzonitic and granitic intrusions associated to the Grenvillian orogeny (Frith and Doig 1973).

The three other localities were all located in the Central Metasedimentary Belt (CMB; Wynne-Edwards 1972; Rivers et al. 1989) of the Grenville Province (Fig. 1). The CMB consists mainly of mafic to felsic metavolcanic and metasedimentary rocks of the Grenville Supergroup intruded by various batholiths and plutons ranging in composition from ultramafic to calc-alkaline (Lumbers 1969; Wynne-Edwards, 1972; Wolff 1982; Pride and

Moore 1983). The volcanic rocks of the Tudor Formation, interpreted as the basal unit of the Grenville Supergroup (Lumbers 1969), have been dated at 1286±15 Ma (Silver and Lumbers 1966). The mafic and felsic plutons of the CMB have yielded Rb-Sr and U-Pb ages ranging from 1220 Ma to 1250 Ma (Krogh and Hurley 1968; Heaman et al. 1984, 1986; Miller 1984).

The magmatic activity was followed by regional metamorphism and deformation events constrained between 1102±4 Ma, the age of a deformed felsic sill and 1088±3 Ma, the age of an undeformed granite (Davis and Bartlett 1988). Uraniferous granites and pegmatites indicate late magmatic activity with Rb-Sr ages ranging from 900 Ma to 1000 Ma in the entire Grenville Province (Fowler and Doig 1982).

The molybdenum deposits in the CMB are not enriched in any other metal than Mo, but are spatially associated with U and Th deposits (Vokes 1963; Karvinen 1973). With the exception of the Moss Mine, most Mo deposits are hosted in stratabound skarns, stratiform hedenbergite paragneisses and unconformable to conformable pegmatite (Karvinen 1973; Carter et al. 1980; Lentz 1991). Molybdenite mineralization in the first two groups are thought to be contemporaneous with an early period of metasomatism, whereas the pegmatite type deposits would have formed during a late period of K and Si metasomatism (Karvinen 1973). However, Lentz (1991) has suggested that all Mo deposits were formed during the same event, based on similar chemical compositions of the mineralized rocks. On the other hand, Lapointe and Gauthier (1992) reported a variety of Mo deposits in the northern part of the CMB that, based on structural relatioships with host rocks, reflects different events.

Sample MG was collected at the Moss Mine, 25 km west of Ottawa (Fig. 1). The gangue consists of greenish feldspar and quartz rock in which pyrite, pyrrhotite, fluorite, magnetite and molybdenite occur partly disseminated or as aggregates. The mine is located in the Onslow syenite, a generally fine-grained, pink, aplite-like rock. The lack of foliation and metamorphism led Vokes (1963) to conclude that the intrusion is late Precambrian. The 883 Ma K-Ar biotite age of the central Onslow complex supports these observations (Doig and Barton 1968).

Samples HM were from the Hunt Mine, a skarn deposit, located 35 km southeast of

Renfrew (Fig. 1). At this locality, a well developed zone of skarn hosting Mo ore was sampled (HM.SK). A zone of marble located inside a pegmatite and hosting veinlets of Mo was also sampled (samples HMG and HMP). The lack of molybdenite in the pegmatite and the fact that the skarn, in several outcrops, is included in, and completely surrounded by pegmatite led Karvinen (1973) to conclude that the mineralization was not associated to the intrusion of the pegmatite.

Samples JTG and JTP were from the Joiner Mine situated in Cardif Township, 25 km northwest of Bancroft (Fig. 1). The property is located on a high ridge consisting of marble and interbedded paragneisses intruded by several sills of monzonite (hedenbergite gneiss) and monzonite pegmatites (Satterly 1960). Although molybdenite appears disseminated in sediments and in the monzonite (Satterly 1960), most of the Mo is found in a coarse augite-feldspar-calcite pegmatite (samples JTG and JTP) showing a concordant contact with the hedenbergite gneiss (Vokes 1963). The close association of the molybdenite and the monzonite rocks suggests that Mo has been concentrated from the hedenbergite gneiss during the formation of the pegmatites (Karvinen 1973; Vokes 1963).

## Analytical techniques

In all deposits except Baie Ste. Catherine, a single grain of molybdenite was withdrawn from the gangue, crushed and sieved to homogeneous grain sizes of 100-60 μm and <60 μm. The Baie Ste. Catherine sample is an aliquot of several disseminated molybdenite grains from a hand-size specimen. Between 25 and 40 mg of molybdenite were washed with distilled water in an ultrasonic bath for 2 minutes and an aliquot of the sample set aside for bulk composition determination. The remaining sample was then sequentially submitted to a differential dissolution treatment using 5% $CH_3COOH$, concentrated HF, 1N HBr, and 2N and 6N HCl. The sequence in which these acids were used is indicated for each sample in Table 1.

After each leaching treatment, the supernate was recovered and the dissolved Pb was processed through anion-exchange separation (Mahnès et al. 1980). When 2 or 3 leaching treatments were done, an aliquot of the residue was dissolved in aqua regia and analyzed and the remaining sample was submitted to additional leaching treatments. Clinopyroxene and K-feldspar were also cleaned with distilled water and leached with HCl and HBr+HF before analysis of the residue. Total blanks were smaller than 50 pg and negligible.

The Pb isotopic compositions were measured using a Faraday detector, except for rare leachates with poorer Pb content that were measured with a Daly detector. Replicate analyses of the NBS SRM-981 standard yielded an overall reproducibility of ±0.1 % $amu^{-1}$ ($2\sigma$) for sample sizes ranging from 5 to 100 ng. All regression treatments were done with the method of York (1969) and the decay constants of Steiger and Jäger (1977). All errors are quoted at the 95% level of confidence.

## Results

The analytical results obtained on all leachates and residues are listed in Table 1 and illustrated in Figs. 2 to 7.

*Massberyl prospect*

Ten determinations of the Pb isotopic composition of leachates and residues were obtained on a molybdenite fraction sieved to 60-100 μm. The Pb isotopic compositions decrease during the leaching treatment yielding $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios in the range of 127.6 to 97.5 and 34.5 to 29.4, respectively (Table 1). These ratios are positively correlated (Fig. 2a) and the slope of the isochron is 0.1731±0.0009 corresponding to an age of 2587±16 Ma. The least radiogenic residue still yielded a very high $^{206}Pb/^{204}Pb$ of 97.5 indicating that the radiogenic Pb component is strongly bound in molybdenite. A K-feldspar grain adjacent to molybdenite was also analyzed. The leachate yielded Pb isotopic compositions similar to that of molybdenite (Table 1) suggesting that traces of molybdenite were dissolved during leaching. The residue yielded Pb isotopic ratios only slightly more radiogenic than typical K-feldspar from unmineralized granitoids in the area (Gariépy and Allègre 1985). Regression of the molybdenite and K-feldspar data yields a slope of

0.1739±0.0005 corresponding to an age of 2595±5 Ma. This suggests that molybdenite and K-feldspar are cogenetic and have the same initial Pb ratios. The $^{238}U/^{204}Pb$ ratio ($\mu$) of molybdenite, calculated using the value of the K-feldspar for initial ratio and the bulk composition, is 228. The data are also positively correlated in a $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (Fig. 2b) along a line corresponding to a Th/U ratio of 0.95±0.02.

*Pidgeon Molydenum Mines*

Two grains were each divided into two size fractions (Table 1). Fractions JPG1 and JPG2 were sieved to a homogeneous grain size while grains JP1 and JP2 were not sieved and are thus of heterogeneous grain size. The most radiogenic composition was obtained from a HF leach of fraction JP1 yielding a $^{206}Pb/^{204}Pb$ ratio of 37.4 while the least radiogenic one was from a residue of the same fraction having a ratio of 25.48 (Table 1). In fractions JP1 and JP2, the Pb isotopic compositions did not decrease regularly during the leaching treatment. This may be explained by the heterogeneous grain size of the fractions, the smaller grains reacting differently to the treatment than the larger ones.

All the results are shown on Fig. 3. The data are positively correlated in the $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (Fig. 3a) but the scatter of the data points greatly exceeds that of analytical precision. The best-fit line drawn through 21 points has a slope of 0.133±0.007 which corresponds to an age of 2.14±0.11 Ga. The results are also poorly correlated in the $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (Fig. 3b); the least radiogenic leachates and residues have an apparent Th/U ratio of 1.2 while this ratio doubles to 2.4 in the most radiogenic samples.

The first HCl leach done on K-feldspar grains has yielded a $^{206}Pb/^{204}Pb$ ratio of 38.8 which is higher than any of the results obtained on molybdenite. However, the second leachate and the residue have isotopic compositions slightly more radiogenic than typical 2.7 Ga old Pb. The K-feldspar results are not collinear with the molybdenite data (Fig. 3a) and define a "two-point isochron" of 2660±10 Ma.

*Baie Sainte-Catherine*

Two fractions of disseminated molybdenite grains were treated separately. Fraction BSCG consisted of 60-100 µm grain while fraction BSC was made of unsieved grains of heterogeneous size. The bulk sample and the leachates yielded $^{206}Pb/^{204}Pb$ ratios of 33.7 to 37.3. However, the residue of fraction BSC yielded $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios much higher than the leachates, but had a comparable $^{208}Pb/^{204}Pb$ ratio (Table 1). This sample was only leached once with HBr and traces of apatite, which is a U-rich but Th-poor mineral, may have been present in the aliquot.

The molybdenite data points are correlated in the isochron diagram (Fig. 4a) yielding an age of 936±120 Ma. Regression of the K-feldspar data with the molybdenite data improves the precision of the age to 931±51 Ma, suggesting that the two phases are cogenetic and that they have the same initial Pb composition. The $\mu$ value calculated for the bulk aliquot of molybdenite is 105±6. The data are also correlated in the $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (Fig. 4b). Assuming that the composition of the K-feldspar is the best estimate of the initial composition of both minerals, the Th/U ratio of $MoS_2$ is 0.77±0.06.

*Moss Mine*

All measurements were done on a 60 to 100 µm grain size fraction. Five leachates and two residues yielded a narrow range of composition with $^{206}Pb/^{204}Pb$ ratios varying only from 19.2 to 21.2 (Table 1). The data are not sufficiently spread in the $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (Fig. 5a) to define a meaningful isochron. However, the molybdenite regression line is parallel to that of the K-feldspars which yield an age of 924±23 Ma. This suggests that the ore has an age comparable to that of the feldspar but that it formed from a fluid phase having a more radiogenic initial Pb isotopic composition. This is also indicated by the relationship between the $^{208}Pb/^{204}Pb$ and the $^{206}Pb/^{204}Pb$ ratios (Fig. 5b). The K-feldpar and the molybdenite data define Th/U ratios of 2.7 and 2.0, respectively, but the molybdenite data are displaced towards a higher initial $^{208}Pb/^{204}Pb$ ratio.

*Hunt Mine*

The analyses were done on a molybdenite grain separated in two size fractions of 60-100 µm (HMG) and <60 µm (HMP). The calcite gangue hosting the ore was also analyzed. The most radiogenic $^{206}Pb/^{204}Pb$ ratios were obtained from a HBr leach while the final residues have yielded the least radiogenic ratios. The molybdenite data define a line of slope equal to 0.0843±0.0024 yielding an age of 1298±53 Ma and is collinear with the calcite gangue (Fig. 6a).

Hedenbergite, K-feldspar and a whole-rock aliquot of a skarn containing disseminated molybdenite were also analyzed. They define a line having a slope of 0.0837±0.00695 corresponding to an age of 1286±75 Ma, but displaced towards lower inital Pb isotopic compositions (Fig. 6a). This suggests that formation of the ore and the skarn were contemporaneous. Assuming that molybdenite had an inital $^{206}Pb/^{204}Pb$ ratio close to that of the K-feldspar residue yields a $^{238}U/^{204}Pb$ ratio of 36.5±1.5 for that mineral.

The silicate minerals, the calcite gangue and the skarn are correlated in the $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram and define a Th/U ratio of ca. 3.5, typical of crustal rocks (Fig. 6b). The molybdenite data define a much lower Th/U ratio of 0.66±0.03, but two HBr leachates have higher $^{208}Pb/^{204}Pb$ ratios suggesting that traces of the carbonate gangue may have been present in the molybdenite sample.

*Joiner Mine*

A single crystal of molybdenite was separated into 2 homogeneous grain size fractions of 60 to 100 μm (JTG) and < 60 μm (JTP). The leaching experiments produced similar results for the two fractions. The most radiogenic $^{206}Pb/^{204}Pb$ ratios came from a HBr leach (JTP), while the least radiogenic values were obtained from residues of both fractions (Table 1).

In the case of these two fractions, silicate material remained in the beakers after complete dissolution of molybdenite in aqua regia. These silicates were made of quartz and/or feldspar containing sulfide impurities. The Pb isotopic composition of the silicates which were included in molybdenite yielded $^{206}Pb/^{204}Pb$ ratios varying from 24.11 to 18.60 (Table 1). There is no clear relationship between the composition of the silicate phases and the corresponding composition of the molybdenite. In a $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram, neither molybdenite nor silicate data are well correlated. The data rather define a band parallel to reference isochrons of 950 Ma (Fig. 7a). Molybdenite data are positively correlated in a $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (Fig. 7b). Some of the silicate data are well correlated with molybdenite while others plot clearly out of the molybdenite trend.

## Discussion

The geological implications of the ages and the initial isotopic compositions obtained on molybdenite ores and associated minerals will be discussed first followed by the geological significance of the Th/U ratios of the molybdenites.

*Massberyl prospect*

The age of 2595±5 Ma obtained for molybdenite and K-feldspar of the Massberyl prospect is younger than that of any intrusive rocks in the area, but comparable to U-Pb ages obtained on hydrothermal rutile and titanite from gold and massive sulfide deposits in the southern Abitibi belt (Schandl et al. 1990; Jemielita et al. 1990; Wong et al. 1991). These U-Pb ages are the youngest found so far in the Abitibi Subprovince and are interpreted to reflect a late hydrothermal event responsible for the mineralization (Jemielita et al. 1990; Wong et al. 1991). The molybdenite age is also similar to $^{40}Ar$-$^{39}Ar$ and Sm-Nd ages obtained on hydrated alteration minerals from the gangue of Au deposits in the Abitibi (Masliwec et al. 1986; Hanes et al. 1989; Anglin 1990) and to muscovite $^{40}Ar/^{39}Ar$ ages from garnet-bearing pegmatites in the area (Feng et al. 1992).

If the isochron defined by K-feldspar and molybdenite data truly represents the intrusion age of the dyke, this would indicate that the 2.6 Ga hydrothermal event responsible for the formation of some of the Abitibi Au deposits may have been driven in places by some magmatic phenomena such as the intrusion of these porphyritic dykes.

Alternatively, the 2.6 Ga Pb-Pb age defined by molybdenite may not represent the "true" crystallization age of the mineral. For example, in areas where the rate of uplift is very slow the Pb-Pb isochron obtained on molybdenite may simply record cooling below a given isotherm, yielding thus apparent ages younger than that of the mineralizing event. Similarly, any younger thermal event bringing molybdenite above its closing temperature of diffusion may partially or totally reset the isotopic system as inferred by Kerrich (1986), Kerrich et al. (1987), and Claoué-Long et al. (1990) for some unusually young U-Pb, Ar-Ar and Sm-Nd ages in the range of 2630 to 2550 Ma obtained on minerals associated with Abitibi gold deposits. Whether some or all of these young ages represents cooling below a particular isotherm, isotopic resetting during reactivation of older structures or the primary ages of gold deposition is still debated (Corfu and Davis 1991; Claoué-Long et al. 1992). The results obtained on molybdenite from the Massbéryl deposits does not discriminate between these possibilities. However, the coincidence between the Pb-Pb age determined here and the $^{40}Ar/^{39}Ar$ muscovite ages reported for Lacorne pegmatites by Feng et al. (1992) suggests that the closure temperature of the U-Pb system in molybdenite is comparable to that of K-Ar in muscovite i.e. close to 350-400°C (Dallmeyer and Keppie 1987).

The time-integrated $^{238}U/^{204}Pb$ ratio of the source reservoir of the Massbéryl dyke is 8.53±0.02. This value is comparable to that determined for late-kinematic, two-mica granitic suites of the Abitibi and Pontiac Subprovinces (Gariépy and Allègre, 1985; Carignan et al. 1992). These systematically yield the most radiogenic initial Pb isotopic compositions and are interpreted to be derived from source areas containing a fair proportion of older crustal precursors (Carignan et al. 1992).

*Pidgeon Molybdenum Mines*

The age of 2.66 Ga obtained for a K-feldspar leachate-residue pair is close to that of late-tectonic granitoid plutons intruding the English River Belt north of the mine (Krogh et al. 1976). However, the apparent age of 2.1 Ga defined by the molybdenite is much younger than that of the host rocks, but ages of ca. 2.1 Ga are not totally unknown in the area. Buchan et al. (1991) reported a U-Pb age of 2.11± 0.05 Ma for the Fort Frances Proterozoic dyke swarms within the Wabigoon and the Quetico subprovinces. Furthermore, Corfu and Wallace (1985) have documented the presence of late Archean zircons, in rhyolites of the Red Lake area north of the Pidgeon mine, having lower Concordia intercept at 2.1 Ga which may be attributed to episodic Pb-loss during thermal reactivation of the rocks. This thermal event may also have been recorded in the Pidgeon molybdenite. If molybdenite and K-feldspar formed at *ca.* 2.7 Ga with the same initial Pb isotopic composition and if molybdenite has been disturbed and isotopically homogeneized at 2.1 Ga, then the initial ratio of molybdenite at the time of the event can be evaluated. This ratio is represented by the intersection of the isochron that developed between 2.7 and 2.1 Ga with the present day molybdenite isochron. The slope of the 2.7 to 2.1 Ga isochron is determined by:

$$(1)\qquad \frac{(^{207}Pb/^{204}Pb)_{T2} - (^{207}Pb/^{204}Pb)_{T1}}{(^{206}Pb/^{204}Pb)_{T2} - (^{206}Pb/^{204}Pb)_{T1}} = \frac{1}{137.88}\frac{(e^{\lambda' T1}-e^{\lambda' T2})}{(e^{\lambda T1}-e^{\lambda T2})}$$

where $T_1$ and $T_2$ the crystallization and crisis ages, respectively and $\lambda$ and $\lambda'$ the decay constants of $^{238}U$ and $^{235}U$. The equation of the present day isochron is:

$$(2)\qquad (^{207}Pb/^{204}Pb)_{T2} = 0.133\ (^{206}Pb/^{204}Pb)_{T2} + 14.209$$

When the composition of the K-feldspar is used for the initial composition of the system at $T_1$, the initial composition of the molybdenite at 2.1 Ga is calculated to be 20.6 for the $(^{206}Pb/^{204}Pb)_{T2}$ ratio and 16.9 for $(^{207}Pb/^{204}Pb)_{T2}$ ratio. These values are lower than any of the results obtained on the residues or leachates and may thus likely represent the actual initial composition of molybdenite at 2.1 Ga. If this is correct, it is then possible to evaluate the $^{238}U/^{204}Pb$ ratio ($\mu$) of molybdenite before and after the event using the compositions of the K-feldspar and of the bulk aliquot. This yields a $\mu_1$ of 47 for the 2.7-2.1 Ga time interval and a $\mu_2$ of 32 for the 2.1-0 Ga period. During the event, molybdenite has thus lost about 30% of its U or gained 30% of its Pb.

*Baie Sainte-Catherine*

The Pb-Pb isochron age of 931±51 Ma obtained for molybdenite and K-feldspar is comparable to the Rb-Sr whole-rock ages determined for late granitoid intrusions in this area of the Grenville Province (Frith and Doig 1973). The time-integrated $^{238}U/^{204}Pb$ ratio for this pegmatite is 8.90±0.05, indicating derivation from a U-rich reservoir. This reservoir may be represented by the mid-Proterozoic paragneisses hosting the Grenvillian granitoid intrusions which have high initial $^{87}Sr/^{86}Sr$ ratios reaching values > 0.720 (Frith and Doig 1973).

*Moss Mine*

The K-feldspar data at the Moss Mine define a Pb-Pb age of 924±23 Ma that is close to the biotite K-Ar age of 883 Ma determined by Doig and Barton (1968). Molybdenite results define a parallel line, suggesting that the ore is of the same age, but displaced towards a higher initial $^{207}Pb/^{204}Pb$ ratio (Fig. 6a). If the higher temperature mineral K-feldspar crystallized first, this can only indicate a change in the nature of the source reservoirs through time: molybdenite was derived either from an older reservoir or from source rocks having a higher U/Pb ratio. Distinct source reservoirs are also indicated in Fig. 6b: molybdenite was derived from a reservoir having a higher $^{208}Pb/^{204}Pb$ ratio, and thus a higher Th/U ratio, than that of K-feldspar. High Th/U ratios are a typical feature of felsic granulite gneisses thought to reflect U migration towards upper crustal levels during regional high-grade metamorphism. This suggests that the fluids responsible for molybdenite precipitation gained their Pb from depleted granulite gneiss while the syenitic magma was derived from more "fertile" source rocks.

*Hunt Mine*

The Pb-Pb isochron ages of 1.30±0.05 and 1.29±0.08 Ga obtained on molybdenite and skarn minerals, respectively, essentially indicate that mineralization was contemporaneous to skarn formation. This supports the model of Karvinen (1973) who thought that the mineralization formed during an early period of metasomatism which preceeded pegmatite intrusion. It also indicates that molybdenite was not heated above its closure temperature during the Grenvillian orogeny. This is unexpected, considering the fact that molybdenite from the Abitibi greenstone belt seems to have a relatively low closure temperature, around 350°-400°C. A possible explanation for this situation would be that, in the Hunt Mine area, the amphibolite facies had been reached prior to or during the formation of the deposit. Another possibility would be that heat alone is not enough to reset the U-Pb system in molybdenite, and that circulating fluids are needed.

However, molybdenite was derived from a source reservoir having time-integrated $^{238}U/^{204}Pb$ ratio (8.78±0.04) slightly higher than that of the skarn (8.68±0.05). Carignan (1989) also reported Pb isotopic data for a variety of marbles from the CMB which were derived from a source reservoir having a mean $^{238}U/^{204}Pb$ ratio of 8.66. This is consistent with the concept that the marbles were the protolith of the skarn and suggest that molybdenite was derived from a distinct, more radiogenic reservoir. In this scenario, molybdenite is a new mineral phase, reflecting the composition of the mineralizing fluids whereas the calc-silicate minerals are metasomatic phases from mixed sources: the marble protolith and the mineralizing fluids. The extent to which the isotopic composition of the protolith will be modified towards that of the fluids will depend on the fluid/rock ratio, and the concentration of Pb in both end-members.

*Joiner Mine*

The results obtained for molybdenite of the Joiner Mine are scattered in the $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (Fig. 7a). The scatter of the data cannot be attributed to secondary perturbation events because, if such was the case, one should observe an equally large dispersion in the $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (Fig. 7b). However, the two analyzed samples contained residual silicates (with sulfide impurities) still present after total dissolution of molybdenite. This was the only case in this study where the analyses were clearly done on mixed mineral populations and this emphasizes one of the limitations of the approach.

Simple mixing of two end-members should nevertheless yield a straight line in the $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram. However, analyses of the silicates show that they have scattered initial Pb isotopic compositions and variable U/Pb ratios. Actually, the inclusions may even represent older xenocrystic material incorporated in the pegmatite dyke. During leaching of molybdenite, Pb was released from the silicates in different proportions, depending on their crystalline integrity and the dissolving strength of the acids used, yielding uncorrelated results. The cause for the better correlation observed in the $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram will be discussed in the next section.

*Th/U ratios of molybdenite*

Some of the Pb-Pb isochrons obtained in this study for molybdenite are in fair agreement with the inferred depositional age of the ore, albeit the ages are not as precise as one would wish. This is probably because molybdenite has a low closure temperature to U and Pb diffusion and is thus sensitive to secondary thermal perturbations. Despite these limitations, the six molybdenite deposits studied here also yielded good to fair alignments in the $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagrams. This places some restrictions on the possibility that micro-inclusions are the carrier of the radiogenic Pb component in this mineral. If present, micro-inclusions must have been represented by a single mineral (in addition to molybdenite): mixtures of three (or more) minerals cannot yield linear trends in the $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram unless two (or more) of the minerals possess identical Th/U ratios (Deloule et al. 1989).

With the exception of the Joiner Mine, the Th/U ratio of molybdenite ranges from 0.7 to 2.0 and is systematically lower than that of most crust-forming silicate rocks (Faure 1986). This indicates that the solid-liquid partition coefficient of Th in molybdenite is much lower than that of U. If this observation of low Th content holds for all Mo deposits, then the correlation between the $^{208}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios in molybdenite and silicates at the Joiner Mine and the high apparent value of the Th/U ratio could be readily explained: during the leaching experiments, the radiogenic $^{208}Pb$ was essentially extracted from the silicate component which is richer in Th.

Considering a negligible fractionation of Th and U between fluids and molybdenite, the U/Pb and Th/U ratios of molybdenite could reflect the nature of fluids involved in the genesis of the deposits. For example, one could speculate that: 1) ortho-magmatic fluids should have U/Pb and Th/U ratios close to that of the mean continental crust, whereas 2) meteoric fluids should have higher U/Pb and lower Th/U ratios, based on the observation that U is considerably more soluble at low temperature than Pb and Th.

The Moss Mine molybdenite, formed in the Onslow syenite body, has U/Pb and Th/U ratios comparable to crust-forming silicate rocks and must have precipitated from ortho-magmatic fluids. In contrast, molybdenite from the skarn deposit of the Hunt Mine and from the Baie Ste.Catherine and Massbéryl pegmatites have low Th/U and high U/Pb ratios. This may characterize molybdenite from late stage magmatic processes and reflect the greater involvement of a meteoric water source.

Molybdenite from the Pidgeon deposit yields variable Th/U ratios that have been approximated by linear regressions: ~1.2 for the least radiogenic samples and ~2.4 for the more radiogenic ones. Assuming that molybdenite has a Th/U ratio of 1.2 and using the value of 20.6 calculated above as its initial $^{206}Pb/^{204}Pb$ composition at 2.1 Ga, its $^{208}Pb/^{204}Pb$ ratio at 2.1 Ga is estimated to be ~33.9. If molybdenite evolved from an initial composition similar to that of K-feldspar, then its Th/U ratio during the 2.7-2.1 Ga time interval was ~0.3, a value that is lower than that of any molybdenite analyzed here. This confirms that molybdenite lost part of its uranium during thermal reset at 2.1 Ga, increasing the apparent Th/U ratio of the mineral thereafter and decreasing the apparent ratio for the time interval of 2.7-2.1 Ga. Uranium loss, relative to Th, would also explain the increase of the apparent Th/U ratio in the more radiogenic aliquots: the latter would have suffered greater U loss due to higher contents.

## Conclusions

This exploratory study of the Pb isotopic systematics in molybdenite from six localities of the Canadian Shield allow to define some general conclusions concerning the behaviour of the U-Th-Pb system in this mineral and to speculate about its potential use to better understand the genesis of molybdenite deposits. These are summarized below:

1) internally consistent Pb-Pb isochrons can be defined for molybdenite using a differential dissolution technique provided that a pure mineral separate is used;
2) the closure temperature of diffusion for the U-Pb system in molybdenite appears to be low and comparable to that of the K-Ar system in muscovite i.e. 350-400°C;
3) molybdenite can be thermally reset, as it occurred at 2.1 Ga for the Pidgeon deposit in the Wabigoon subprovince.
4) thermal resetting of molybdenite appears to induce a larger loss of uranium relative to Pb and Th;
5) the Th/U ratio of molybdenite is systematically lower than 2.0 which probably indicates that the solid-liquid partition coefficient of Th in molybdenite is much lower than that of U;
6) it is possible that molybdenite from late-stage magmatic deposits like pegmatites or skarns is characterized by very high $^{238}U/^{204}Pb$ ratios (30-230) and very low Th/U ratios (0.7-1.2) which may reflect the greater involvement of a meteoric water source;
7) in all the studied deposits molybdenite was derived from source reservoirs having

relatively high time-integrated $^{238}U/^{204}Pb$ ratios.

## Acknowledgments

This study was supported by a research agreement from Energy, Mines and Resources Canada and by operating grants (CG) and post-graduate scholarships (JC) from the Natural Sciences and Engineering Council (NSERC) of Canada and from the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (FCAR) of Québec. Laboratory costs at GEOTOP are partially supported by infrastructure grants from NSERC and FCAR.

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## Figure captions

Fig. 1. Location of the studied molybdenum deposits. PM = Pidgeon Molybdenum Mine; MB = Massbéryl; BSC = Baie Ste. Catherine; Moss; HM= Hunt Mine; JT = Joiner deposits.

Fig. 2. Pb isotopic data for molybdenite and K-feldspar from the Massbéryl deposit shown in a) $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ and b) $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagrams. The Th/U ratio was calculated using an age of 2595 Ma.

Fig. 3. Pb isotopic data for molybdenite and K-feldspar from the Pidgeon Molybdenum deposit shown in a) $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ and b) $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagrams. The Th/U ratios were calculated using an age of 2.14 Ga.

Fig. 4. Pb isotopic data for molybdenite and K-feldspar from the Baie Ste. Catherine showing shown in a) $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ and b) $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagrams. The Th/U ratio was calculated using an age of 0.93 Ga.

Fig. 5. Pb isotopic data for molybdenite and K-feldspar from the Moss Mine shown in a) $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ and b) $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagrams. The Th/U ratio was calculated using an age of 924 Ma.

Fig. 6. Pb isotopic data for molybdenite and skarn minerals and whole rock from the Hunt deposit shown in a) $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ and b) $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagrams. The Th/U ratios were calculated using an age of 1.3 Ga.

Fig. 7. Pb isotopic data for molybdenite and silicate inclusions from the Joiner deposit shown in a) $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ and b) $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagrams. Isochrons of 950 Ma are shown for reference in Fig. 7a.

Table 1. Pb isotopic composition of molybdenite and minerals.

| Locality<br>Sample | Leach | Acid<br>Size | $^{206}Pb/^{204}Pb$ | $^{207}Pb/^{204}Pb$ | $^{208}Pb/^{204}Pb$ |
|---|---|---|---|---|---|
| **Massbéryl prospect** | | | | | |
| MB | B | 60-100 µm | 127.263 | 34.525 | 63.683 |
| MB.1 | L1 | Acetic | 121.869 | 33.662 | 61.892 |
| MB.2 | L2 | HBr | 126.589 | 34.372 | 63.236 |
| MB.3 | R1 | | 126.668 | 34.351 | 63.550 |
| MB.4 | L3 | HBr | 127.612 | 34.428 | 63.542 |
| MB.5 | L4 | HBr | 127.047 | 34.405 | 63.552 |
| MB.6 | L5 | HBr | 122.070 | 33.625 | 61.787 |
| MB.7 | R2 | | 122.745 | 33.688 | 62.106 |
| MB.8 | L6 | HCl | 124.203 | 33.901 | 62.404 |
| MB.9 | L7 | HBr | 101.184 | 29.881 | 56.969 |
| MB.10 | R3 | | 97.509 | 29.356 | 56.055 |
| MB.KF1 | L1 | HCl | 122.795 | 33.516 | 62.210 |
| MB.KF3 | R1 | | 14.184 | 14.777 | 33.424 |
| **Pidgeon Mine** | | | | | |
| JPG | B | | 32.178 | 18.457 | 38.923 |
| JPG1.1 | L1 | Acetic | 35.849 | 18.918 | 41.018 |
| JPG1.2 | L2 | HBr | 32.922 | 18.890 | 40.351 |
| JPG1.3 | R1 | | 27.198 | 17.655 | 35.947 |
| JPG2.1 | L1 | Acetic | 36.608 | 19.001 | 41.911 |
| JPG2.2 | L2 | HF | 34.816 | 18.854 | 40.849 |
| JP | B | | 32.872 | 18.565 | 37.341 |
| JP1.1 | L1 | Acetic | 34.592 | 18.803 | 39.818 |
| JP1.2 | L2 | HF | 37.399 | 19.091 | 41.218 |
| JP1.3 | L3 | 2N HCl | 35.382 | 19.019 | 40.159 |
| JP1.4 | R1 | | 28.013 | 17.936 | 36.151 |
| JP1.5 | L4 | 2N HCl | 28.041 | 17.806 | 36.621 |
| JP1.6 | R2 | | 25.481 | 17.492 | 35.693 |
| JP1.7 | L5 | 6N HCl | 30.481 | 18.452 | 36.574 |
| JP1.8 | L6 | 6N HCl | 27.409 | 17.857 | 36.618 |
| JP2.1 | L1 | Acetic | 29.870 | 18.167 | 37.378 |
| JP2.2 | L2 | HF | 36.650 | 18.893 | 40.610 |
| JP2.3 | L3 | 2N HCl | 36.706 | 19.019 | 39.727 |
| JP2.4 | R1 | | 27.952 | 17.861 | 36.262 |
| JP2.5 | L4 | 2N HCl | 31.453 | 18.548 | 37.518 |
| JP2.6 | R2 | | 32.113 | 18.763 | 38.111 |
| JP.KF1 | L1 | 6N HCl | 38.819 | 19.312 | 45.781 |
| JP.KF2 | L2 | HF+HBr | 14.466 | 14.879 | 33.665 |
| JP.KF3 | R1 | | 14.662 | 14.949 | 33.533 |
| **Baie Ste. Catherine** | | | | | |
| BSC | B | | 35.009 | 16.780 | 40.930 |
| BSC.1 | L1 | HBr | 37.322 | 17.029 | 41.397 |

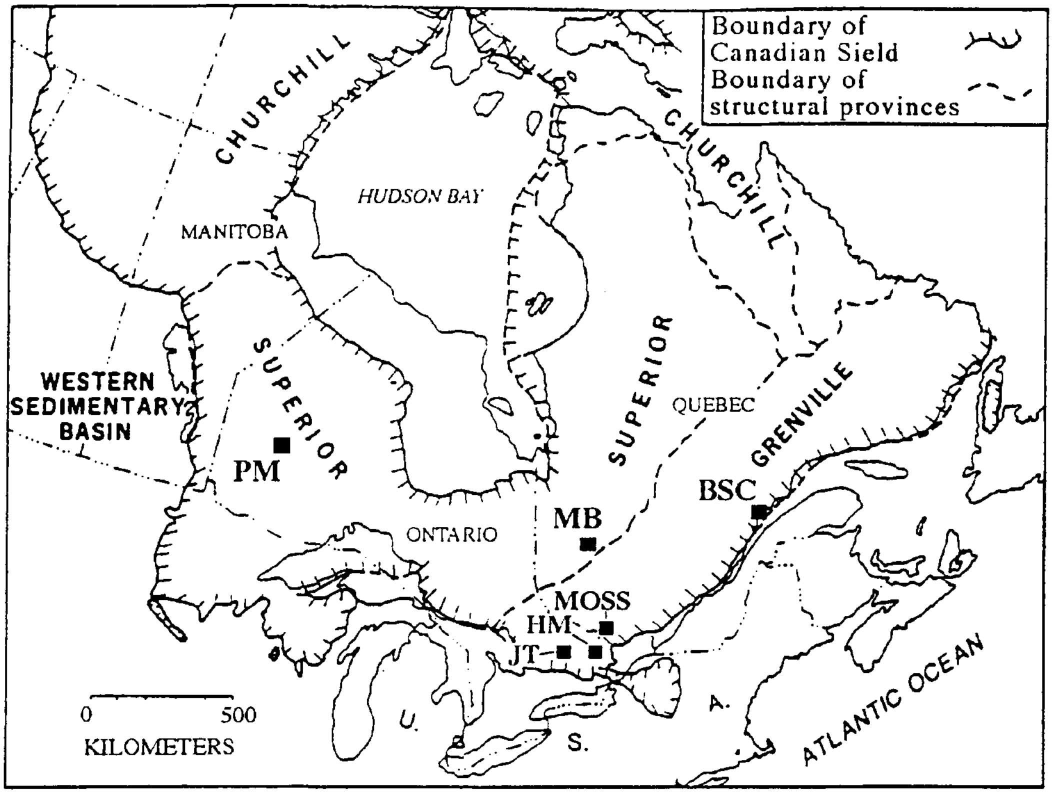
Table 1. Pb isotopic composition of molybdenite and minerals (continued).

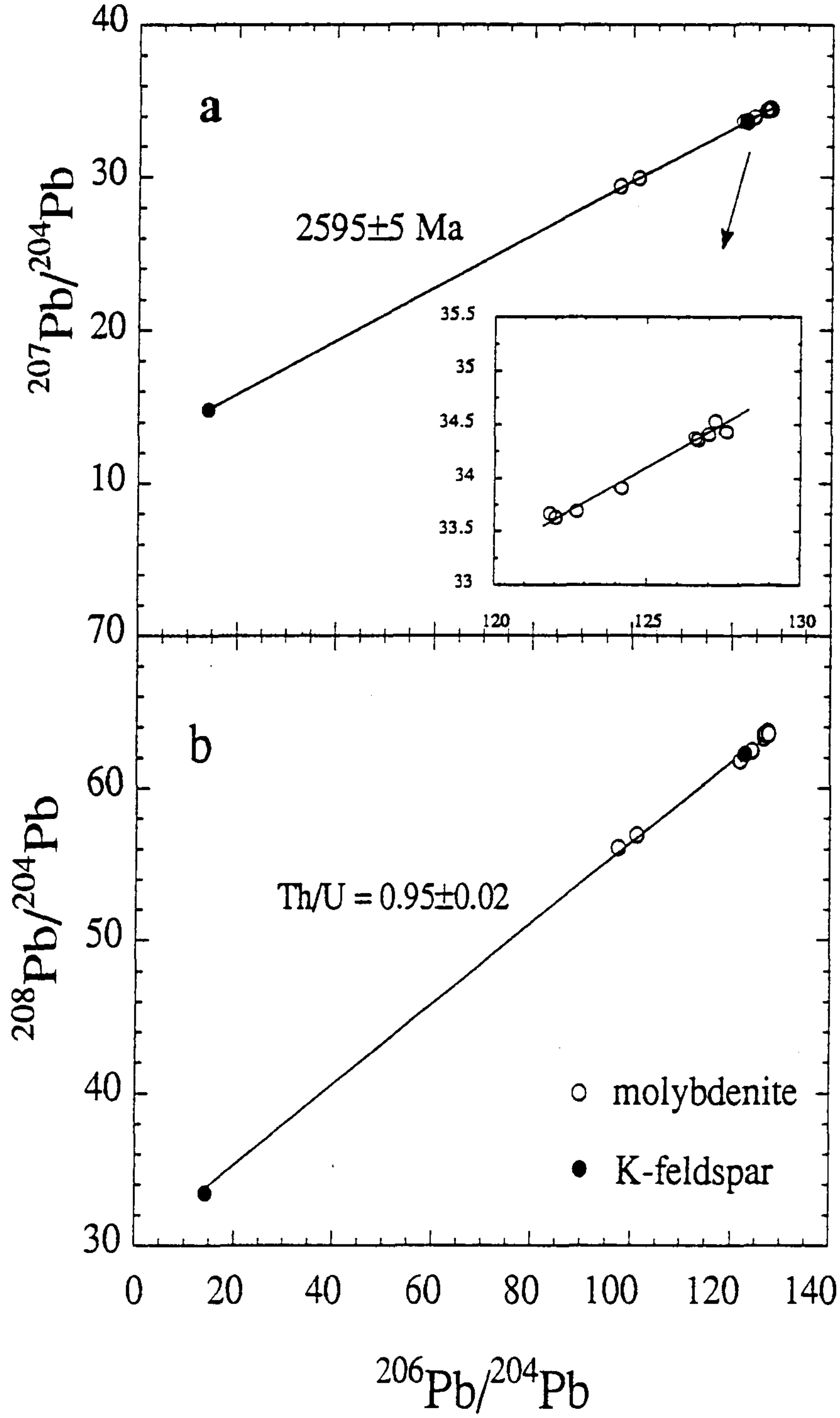
| Locality Sample | Leach | Acid Size | $^{206}Pb/^{204}Pb$ | $^{207}Pb/^{204}Pb$ | $^{208}Pb/^{204}Pb$ |
|---|---|---|---|---|---|
| **Baie Ste. Catherine** | | | | | |
| BSC.2 | L2 | HBr | 36.516 | 17.011 | 41.473 |
| BSCG.1 | L1 | HBr | 33.730 | 16.685 | 40.100 |
| BSCG.2 | R1 | | 52.902 | 18.070 | 40.165 |
| BSCG.FK1 | L1 | 6N HCl | 19.411 | 15.756 | 38.016 |
| BSCG.FK3 | R1 | | 18.273 | 15.669 | 37.099 |
| **Moss Mine** | | | | | |
| MGG.1 | L1 | Acetic | 20.213 | 15.706 | 40.096 |
| MGG.2 | L2 | HBr | 20.850 | 15.726 | 40.850 |
| MGG.3 | R1 | | 19.238 | 15.620 | 39.984 |
| MGG.4 | L3 | HBr | 21.176 | 15.705 | 41.002 |
| MGG.5 | L4 | HBr | 20.957 | 15.718 | 40.878 |
| MGG.6 | L5 | HCl | 20.609 | 15.735 | 40.789 |
| MGG.7 | R2 | 60-100 μm | 21.846 | 15.809 | 41.588 |
| MGG.KF1 | L1 | 6N HCl | 25.148 | 15.972 | 43.047 |
| MGG.KF2 | L2 | HF+HBr | 18.663 | 15.523 | 37.756 |
| MGG.KF3 | R1 | | 18.001 | 15.470 | 37.175 |
| **Hunt Mine** | | | | | |
| HMG | B | 60-100 μm | 25.607 | 16.212 | 37.653 |
| HMG.1 | L1 | Acetic | 24.316 | 16.145 | 37.474 |
| HMG.2 | L2 | HBr | 28.424 | 16.437 | 38.116 |
| HMG.3 | R1 | | 22.759 | 15.969 | 37.231 |
| HMG.4 | L3 | HBr | 26.651 | 16.276 | 39.336 |
| HMG.5 | L4 | HBr | 24.559 | 16.102 | 38.538 |
| HMG.6 | R2 | | 22.438 | 15.953 | 37.040 |
| HMP.1 | L1 | Acetic | 25.352 | 16.196 | 37.736 |
| HMP.2 | L2 | HBr | 28.702 | 16.508 | 38.382 |
| HMP.3 | R1 | < 60 μm | 22.533 | 15.918 | 36.986 |
| HM.CAL | B | | 18.833 | 15.614 | 37.826 |
| HM.SK | B | | 20.187 | 15.715 | 39.086 |
| HM.PX | L1 | HCl | 21.013 | 15.763 | 40.825 |
| HM.PX | R1 | | 17.884 | 15.500 | 37.246 |
| HM.KF1 | L1 | HCl | 19.340 | 15.629 | 39.044 |
| HM.KF2 | L2 | HF+HBr | 18.110 | 15.559 | 37.051 |
| HM.KF3 | R1 | | 17.458 | 15.461 | 36.856 |
| **Joiner Mine** | | | | | |
| JTG | B | | 23.266 | 15.856 | 42.206 |
| JTG.1 | L1 | Acetic | 22.707 | 15.818 | 41.417 |
| JTG.2 | L2 | HBr | 24.295 | 15.942 | 42.905 |
| JTG.3 | R1 | | 21.934 | 15.738 | 40.569 |
| JTG.4 | L3 | HBr | 23.030 | 15.906 | 41.715 |
| JTG.5 | L4 | HBr | 22.995 | 15.974 | 41.686 |

Table 1. Pb isotopic composition of molybdenite and minerals (continued).

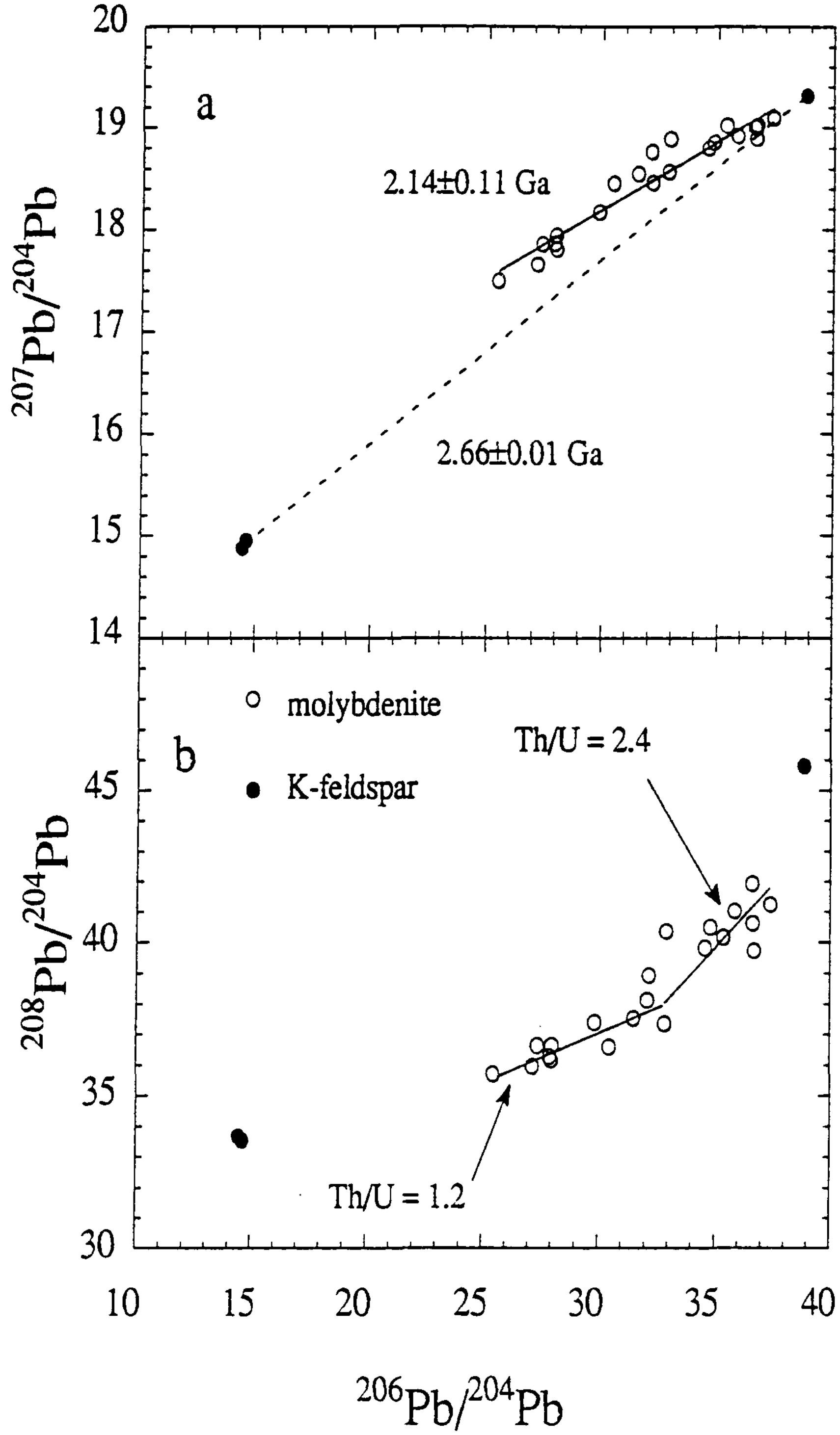
| Locality Sample | Leach | Acid Size | $^{206}Pb/^{204}Pb$ | $^{207}Pb/^{204}Pb$ | $^{208}Pb/^{204}Pb$ |
|---|---|---|---|---|---|
| **Joiner Mine** | | | | | |
| JTG.6 | R2 | | 21.561 | 15.809 | 40.531 |
| JTG.7 | R3 | | 21.905 | 15.842 | 40.860 |
| JTP.1 | L1 | Acetic | 26.117 | 15.061 | 44.457 |
| JTP.2 | L2 | HBr | 26.369 | 16.085 | 44.474 |
| JTP.3 | R1 | | 21.638 | 15.799 | 40.493 |
| JTG.INC | B | | 19.362 | 15.669 | 38.646 |
| JTG.INC3 | B | | 22.347 | 15.824 | 40.573 |
| JTG.INC6a | L1 | HCl | 18.595 | 15.654 | 38.160 |
| JTG.INC6b | R1 | | 24.109 | 15.917 | 41.769 |
| JTG.INC7a | L1 | HF-HBr | 20.464 | 15.758 | 39.686 |
| JTG.INC7b | R1 | | 21.401 | 15.819 | 40.296 |
| JTP.INC3 | B | | 21.136 | 15.729 | 39.212 |

KF: K-feldspar; PX: pyroxene; CAL: calcite gangue; SK: skarn;
INC: silicate inclusions; B: bulk sample; L: leachate; R: residue;

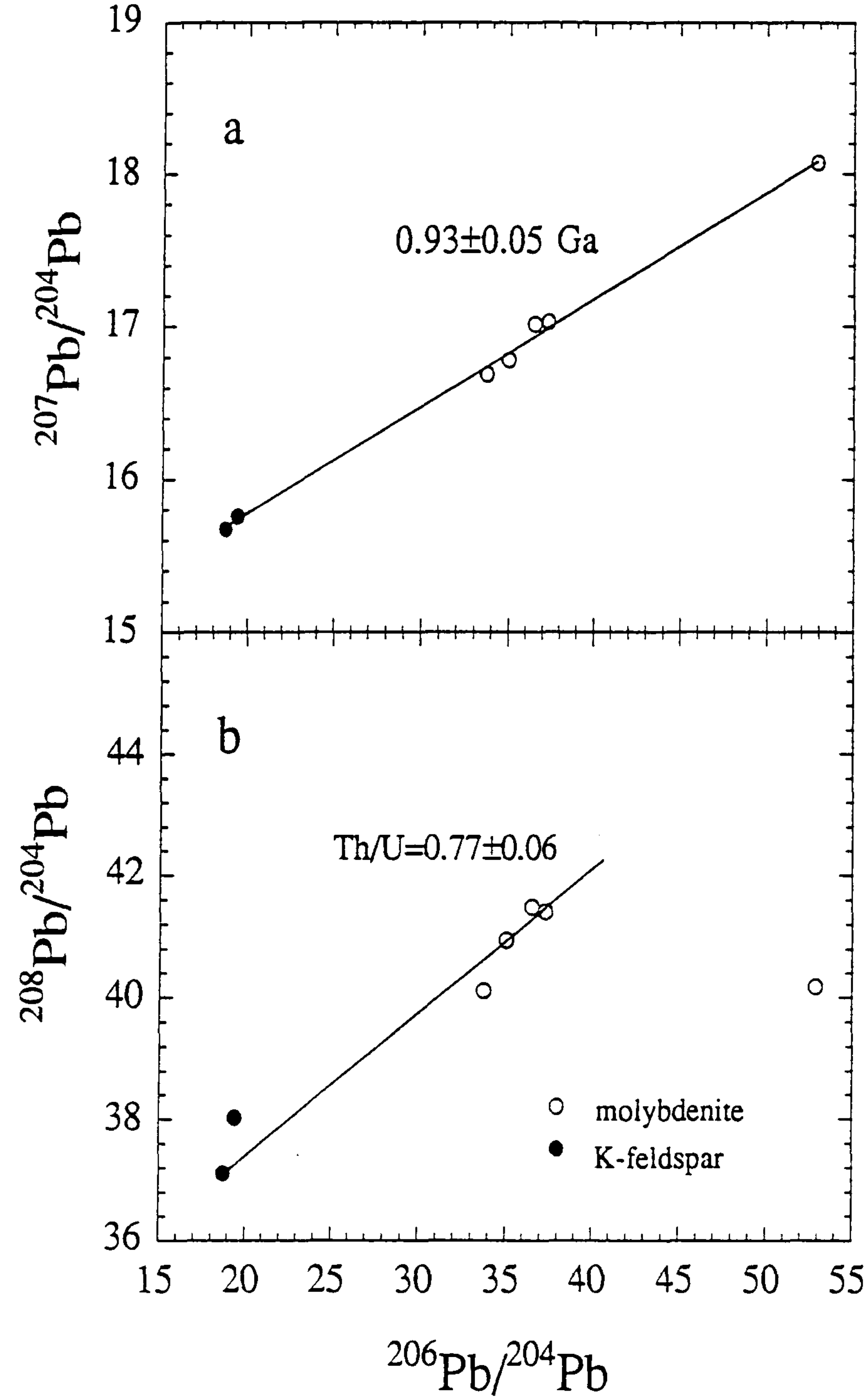

Boundary of
Canadian Sield
Boundary of
structural provinces
CHURCHILL
CHURCHILL
HUDSON BAY
MANITOBA
SUPERIOR
SUPERIOR
QUEBEC
GRENVILLE
WESTERN
SEDIMENTARY
BASIN
PM
ONTARIO
MB
BSC
MOSS
HM
JT
0
500
KILOMETERS
U.
S.
A.
ATLANTIC OCEAN



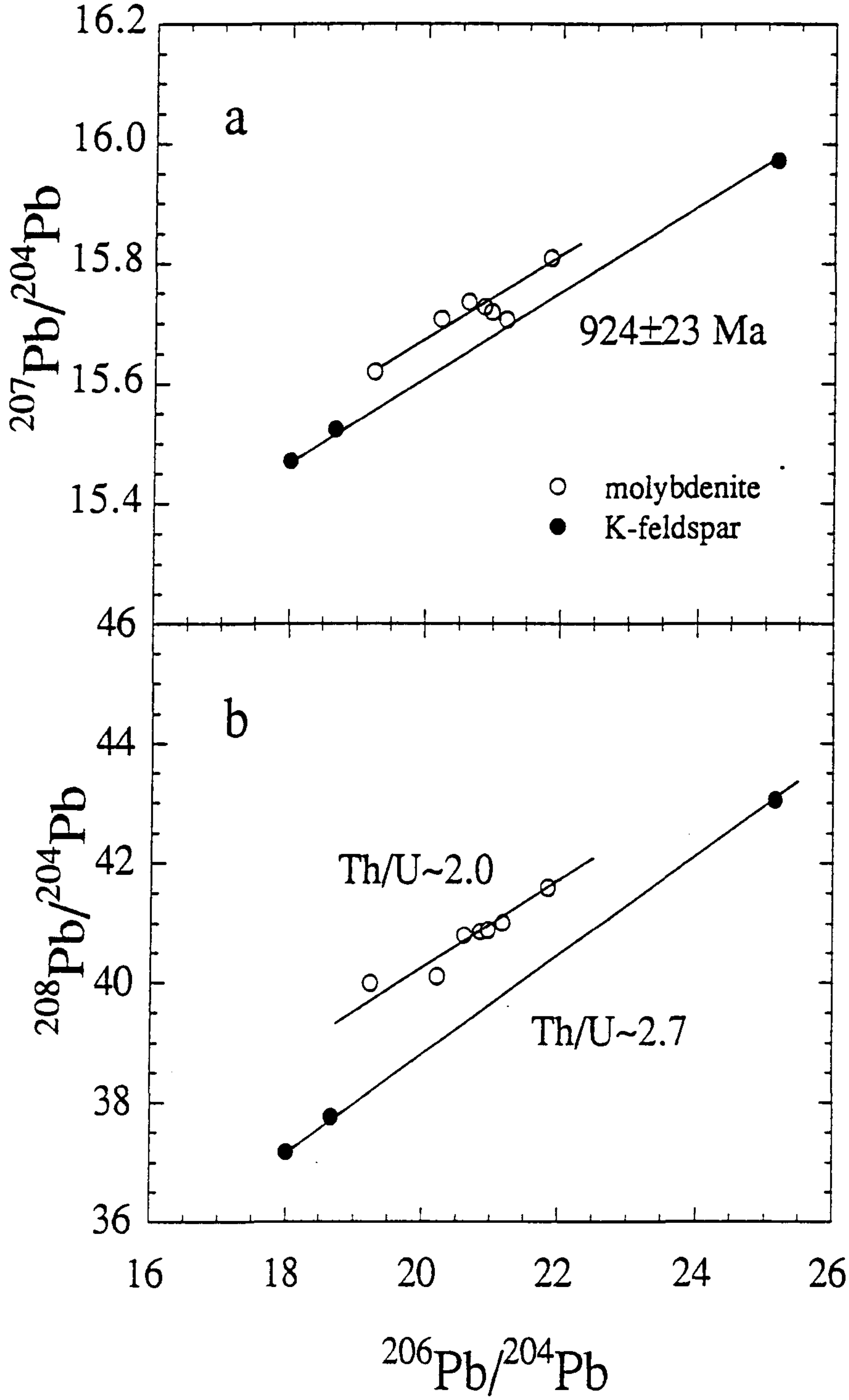
a
2595±5 Ma
b
Th/U = 0.95±0.02
molybdenite
K-feldspar
$^{207}Pb/^{204}Pb$
$^{208}Pb/^{204}Pb$
$^{206}Pb/^{204}Pb$



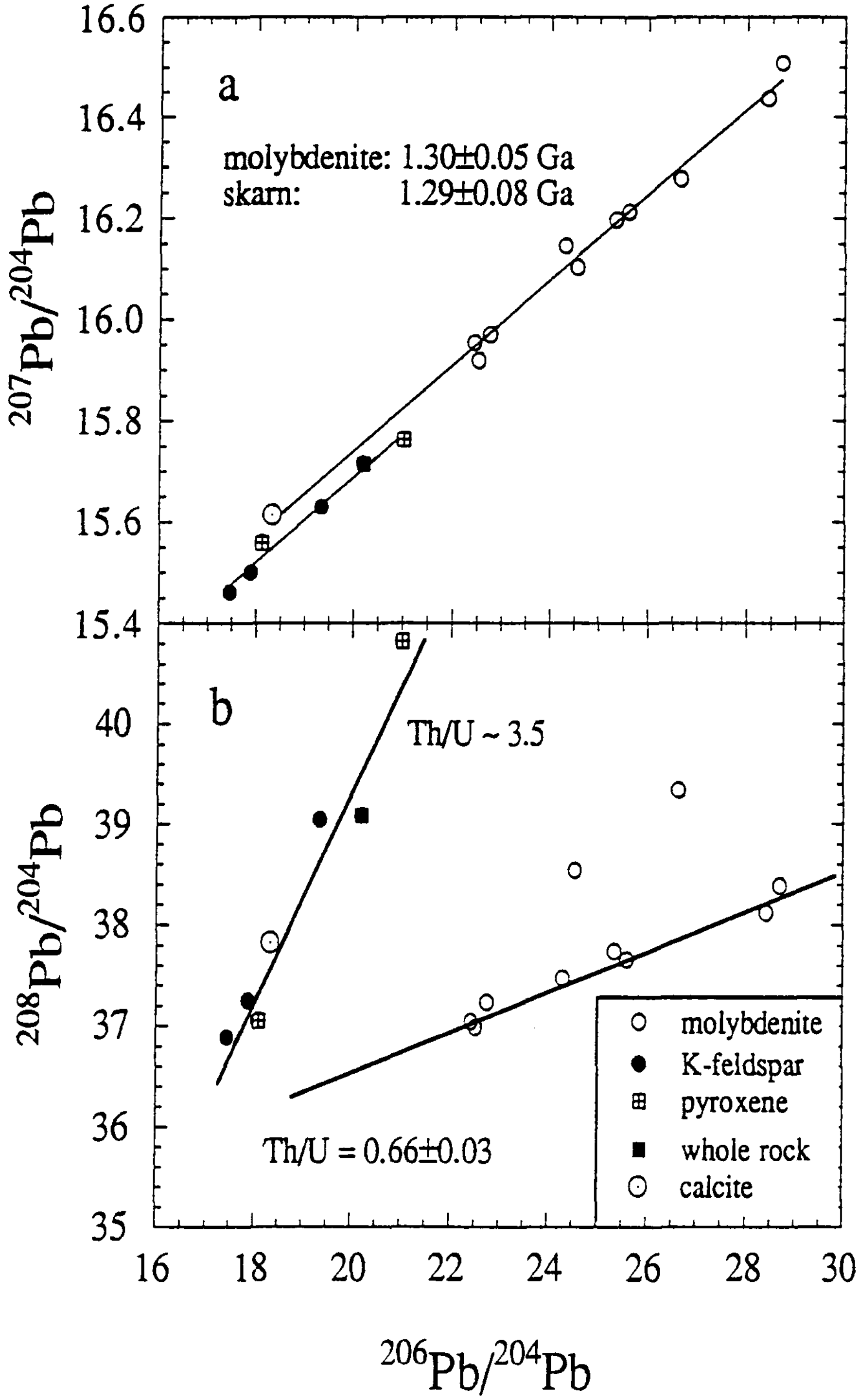
20
19
18
17
16
15
14
a
2.14±0.11 Ga
2.66±0.01 Ga
$^{207}Pb/^{204}Pb$
molybdenite
K-feldspar
b
Th/U = 2.4
Th/U = 1.2
45
40
35
30
$^{208}Pb/^{204}Pb$
10
15
20
25
30
35
40
$^{206}Pb/^{204}Pb$

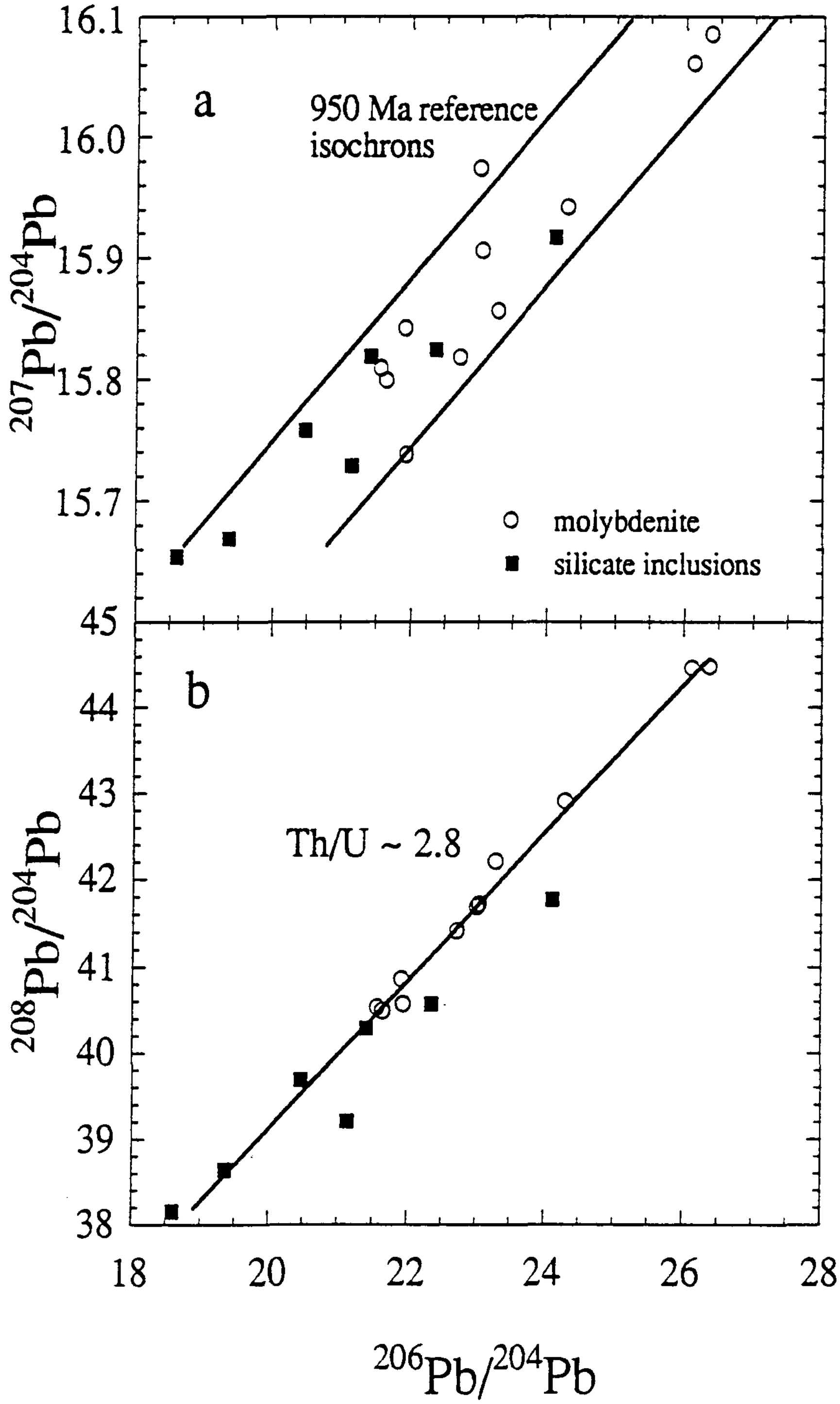


a
0.93±0.05 Ga
$^{207}Pb/^{204}Pb$
19
18
17
16
15
b
Th/U=0.77±0.06
$^{208}Pb/^{204}Pb$
44
42
40
38
36
molybdenite
K-feldspar
15
20
25
30
35
40
45
50
55
$^{206}Pb/^{204}Pb$



a
924±23 Ma
molybdenite
K-feldspar
b
Th/U~2.0
Th/U~2.7
$^{207}Pb/^{204}Pb$
$^{208}Pb/^{204}Pb$
$^{206}Pb/^{204}Pb$
16.2
16.0
15.8
15.6
15.4
46
44
42
40
38
36
16
18
20
22
24
26


a
molybdenite: 1.30±0.05 Ga
skarn: 1.29±0.08 Ga
b
Th/U ~ 3.5
Th/U = 0.66±0.03
molybdenite
K-feldspar
pyroxene
whole rock
calcite
207Pb/204Pb
208Pb/204Pb
206Pb/204Pb
16.6
16.4
16.2
16.0
15.8
15.6
15.4
40
39
38
37
36
35
16
18
20
22
24
26
28
30



16.1
16.0
15.9
15.8
15.7
a
950 Ma reference isochrons
molybdenite
silicate inclusions
$^{207}Pb/^{204}Pb$
45
44
43
42
41
40
39
38
b
Th/U ~ 2.8
$^{208}Pb/^{204}Pb$
18
20
22
24
26
28
$^{206}Pb/^{204}Pb$

# U-Pb isotope geochemistry of molybdenum deposits from the Preissac-Lacorne-Lamotte intrusive complex, southern Abitibi belt: evidence for late and post-Archean thermal events

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## Abstract

Molybdenite and gangue minerals from four molybdenum deposits within the Preissac-Lacorne-Lamotte intrusive complex of the southern Abitibi greenstone belt have been analyzed for their Pb isotopic compositions. The Pb and U concentrations were also determined for molybdenite from these deposits and from the nearby Massbéryl deposit. In most cases, a differential dissolution technique applied on molybdenite yield very radiogenic compositions leading to a spread in analytical results sufficiently large to define meaningful Pb-Pb ages. Ages in the range of 2.56 to 2.60 Ga obtained for three out of five deposits can be related to regional thermal pulses affecting the late Archean Abitibi greenstone belt well after the termination of the magmatic cycles. Younger ages of *ca.* 2.5, 2.3 and 1.75 Ga were also recorded and are related to episodic thermal perturbations corresponding respectively to the intrusion of the Matachewan and Preissac-Nipissing dykes, and to the alteration of the Nipissing dykes.

Molybdenite is always deficient in uranium compared to Pb, (up to 99% deficient) and, as a consequence, cannot be dated by the U-Pb method. The deficiency in uranium is best explained by recent U-loss in response to changes in the redox and pH conditions induced by meteoric water circulation.

## Introduction

Molybdenite is a mineral that frequently has very radiogenic Pb-isotopic compositions corresponding to time-integrated $^{238}U/^{204}Pb$ ratios ($\mu$) ranging from 20 to more than 200 (Carignan and Gariépy 1992). Pb-isotopic analyses of molybdenite and other sulfides from several deposits in the Canadian Shield have yielded internally consistent Pb-Pb isochron ages that are in fair agreement with inferred ages of mineralization. Carignan and Gariépy (1992) have shown that the closure temperature of diffusion for the U-Pb system in molybdenite is low (< 350-400°C ?). They also shown that thermal resetting of this mineral appears to induce a larger loss of uranium relative to Pb and Th. In addition, Carignan and Gariépy (1992) showed that the Th/U ratio of molybdenite is systematically lower than 2.0 which probably indicates that the solid-liquid partition coefficient of Th in molybdenite is much lower than that of U. Finally, these authors speculated that the very high $^{238}U/^{204}Pb$ ratios (30-230) and very low Th/U ratios (0.7-1.2) in molybdenite from late-stage magmatic deposits like pegmatites or skarns may reflect a greater involvement of a meteoric water source.

Luck and Allègre (1982) also presented evidence for open system behaviour of the Re-Os isotope system in molybdenite. These authors obtained a mean age of 6.5 Ga for molybdenite of the Lacorne pluton in the southern Abitibi greenstone belt. The unusually high apparent age is thought to reflect loss of the parent isotope of Re, during post-crystallization thermal reactivation, but significantly little or no loss of Os (the daughter isotope), (Luck and Allègre 1982). Actually, the open system behavior of the Re-Os system in molybdenite appears to be a common feature as Luck et al. (1983) have reported a number of ages for molybdenite deposits of the western North America, that are systematically older than those of their host rocks. In this area, it is necessary to invoke up to 70% of Re-loss to explain the difference between the apparent and the actual age of mineralization.

Thus, Re-Os system in all molybdenites from the southern Abitibi belt may have been partially or totally reset by younger thermal events while the U-Pb system was not. Another possibility would be that both systems were perturbated but not in all molybdenites, in response to heat and fluid circulation. In such a case, the study of U-Pb systematics in molybdenite could become a window on the late hydrothermal history of the southern Abitibi belt. Thus, the aim of this study is to document the behavior of the U-Pb system in molybdenite and its potential to act as a geochronometer capable of dating U-rich sulfides. Work was focused on the Lacorne block in the southern part of the belt, because it contains a large number of Mo deposits and the isotopic composition of potential Pb reservoirs has been thoroughly evaluated (Carignan et al. 1992a).

## Geological setting and sampling

The granitoid bodies within the Preissac-Lacorne-Lamotte complex intrude in ultramafic and basaltic volcanic rocks, and minor metasedimentary rocks (Fig.1). Some volcanic rocks south of the complex, in the Val d'Or area, have been dated with the U-Pb method at 2705±1 Ma (Wong et al. 1991). The Preissac and Lamotte intrusives are part of a suite of post-kinematic K-rich plutons that have been classified by Rive et al. (1990) as belonging to suite H and consisting of granodiorites, muscovite-biotite monzogranites and pegmatites. Their initial Pb-isotopic compositions suggest that they were generated through melting of pre-existing crustal materials (Carignan et al. 1992a). The Lacorne pluton is a calc-alkaline body classified as belonging to suite F (Rive et al. 1990). It has been studied in detail by Bourne and Danis (1987) who subdivided it into three compositional zones ranging from: (1) hornblende-biotite gabbro breccia to monzonite; (2) biotite-hornblende diorite to granodiorite; and (3) muscovite-biotite-garnet leuco-monzogranite. The first two zones have all the characteristics of suite F and are thought to be older than the third zone, found in the northern part of the pluton (Boily et al. 1990), which is analogous to suite H.

Thermobarometric data for garnet-muscovite granites and pegmatites of suite H (Feng and Kerrich 1990) indicate that pressures between 5 and 3.6 Kbars and temperatures from 800°C to 550°C prevailed during the emplacement of the plutons. However, the monzodiorite-monzonite-granodiorite series typical of suite F has yielded lower pressure conditions of 1.5 to 0.9 Kbars which is interpreted to reflect intrusion during the progressive uplift of the block (Feng and Kerrich 1990). If this is correct, plutons of suite F should be younger than those of suite H. However, the suite H plutons appear to be systematically younger than all other intrusives in the Abitibi belt. Machado et al. (1992) reported a monazite U-Pb age of 2641±2 Ma for the Lamotte pluton. The Preissac pluton has yielded a U-Pb age of 2655 +65/-25 Ma (Steiger and Wasserburg 1969) and a Pb-Pb mineral isochron age of 2694±40 Ma (Gariépy and Allègre 1985). Feng and Kerrich (1991) and Feng et al. (1992), using the single zircon evaporation technique, reported minimum $^{207}Pb/^{206}Pb$ ages ranging from 2632 Ma to 2644 Ma for K-rich granites and pegmatites in the area.

The Preissac-Lacorne-Lamotte complex differs from the rest of the Abitibi belt by its high concentration of Mo-Li-Be deposits, its higher metamorphic grade and the absence of gold mineralization (Feng et al. 1992). In most cases, molybdenum ores are confined to hydrothermal quartz veins in which late K-feldspar, muscovite and molybdenite were introduced along vertical and sub-horizontal fractures crosscutting the plutons (Norman 1945; Taner 1989). Molybdenite may also occur in pegmatite dykes and quartz veins either found at the intrusion edges (Leduc 1980) or crosscutting surrounding metavolcanic and metasedimentary rocks (see Vokes 1963 and Boily et al. 1990 for details). Molybdenite occurs frequently as rosettes intergrown with muscovite and alkali feldspar suggesting that these minerals were precipitated simultaneously (Mulja et al. 1990).

Five types of fluid inclusions have been identified in quartz from the Moly Hill Mine, a typical deposit of the Preissac intrusion which were grouped into two populations (Mulja et al. 1990) on the basis of their temperature of homogeneization ($T_h$): (1) high temperature ($T_h$: 325-450°C) and high salinity (15-25 wt.% NaCl eq.), and (2) low temperature ($T_h$: 150-200°C) and low salinity (<10 wt.% NaCl eq.). Molybdenite is thought to have precipitated from the higher temperature orthomagmatic fluids during cooling (Mulja et. al 1990).

Samples were taken from five deposits including two major mines where molybdenum had been extracted until the late fifties and early sixties (Fig. 1). The Preissac and the Cadillac Mines (hereafter labelled PM and CM, respectively) are located in the Preissac pluton (Fig. 1). Samples IPM, IIIPM, IVPM and IICM were taken from stockwork facies developed within K-feldspar-quartz-muscovite pegmatites while samples IIPM, ICM and IIICM were from massive quartz veins bearing coarse flakes of molybdenite. At these mines, studies of quartz fluid inclusions (Taner 1989) indicate that the mineralizing fluids were highly to moderately saline (18-26 wt.% NaCl eq.) and had a mixed magmatic-meteoric origin. Temperature and pressure conditions were about 425°C and 740-680 bars (Taner 1989). These pressures are much lower than those determined by Feng and Kerrich (1990) for rocks of the host plutons suggesting either that the mineralization formed during the latest magmatic stages (1.5-0.9 Kbars ?) or that it is related to an independent younger thermal event. The Heigh of Land prospect (sample HL) is located at the western margin of the Lamotte pluton (Fig. 1). It consists of disseminated molybdenite flakes within a quartz-muscovite vein. The La Pause prospect (sample LP) is situated at the western edge of the complex, south of the La Pause intrusion (Fig. 1). It consists of molybdenite veinlets within a quartz-K-feldspar-muscovite pegmatite. Secondary iron oxides are observed along the fractures hosting the mineralization. Finally, the Massberyl deposit consists of a muscovite-garnet-K-feldspar-spodumene dyke found in the northern part of the Lacorne pluton.

## Analytical techniques

Pb isotopic analyses have been done on different mineral phases such as molybdenite, K-feldspar, muscovite and quartz. In each sample, one molybdenite grain (2.5 to 12 mg) was crushed and sieved to a homogeneous grain size fraction of 100 to 200 μm. A differential dissolution treatment (Carignan and Gariépy 1992) was then applied to this powder and, inasmuch as possible, six analyses were obtained corresponding to the following sequence: (1) bulk sample; (2) 5% acetic acid leach; (3) 0.8N hydrobromic acid leach; (4) residue #1; (5) 6N HCl leach; and (6) residue #2. Leaching was done at 90°C for 30 ($CH_3COOH$ and HCl) or 60 (HBr) minutes. K-feldspar (5-10 mg) and quartz (180 mg) were washed in hot 6N HCl for 12 hours, rinsed with distilled water, powdered and leached with a diluted HF-HBr solution for 30 minutes. The supernate was recovered for analysis and the residue was dissolved in hot HF-$HNO_3$ solution. Muscovite (80 mg) was leached twice in hot 6N HCl and 7N $HNO_3$ for 12 hours before final dissolution. The U and Pb contents of molybdenite were determined by isotope dilution using a mixed $^{205}Pb$-$^{233}U$-$^{235}U$ spike on aliquots (0.8 to 4.7 mg) of the untreated bulk samples.

Separation of Pb for mass spectrometric analysis was done using the technique of Mahnès et al. (1980) and a HCl chemistry was used to purify U. Total Pb and U blanks were smaller than 30 and 5 pg, respectively. Regression treatments were done with the method of York (1969) and the decay constants of Steiger and Jäger (1977). All errors are quoted at the 95% level of confidence.

## Results

The Pb-Pb and U-Pb analytical results are listed in Tables 1 and 2, respectively, and illustrated in Figs. 2 to 6.

*Preissac Mine*

Results were obtained for 4 different samples from the mine. Molybdenite from these samples is very radiogenic with $^{206}Pb/^{204}Pb$ ratios ranging from 30.3 to 74.9 (Table 1). Sample IPM was a granitic pegmatite with coarse molybdenite grains. The analytical results for leachates and residues of molybdenite are positively correlated in the $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ (Fig. 2a) along a line of slope equal to 0.1629±0.0014 (MSWD = 5.4) which would correspond to an age of 2486±50 Ma. Results for leachates and residues of 2 K-feldspar (KF) fractions from the same sample are also shown on Fig. 2a. They fit a line having a slope of 0.1645±0.0054 (MSWD = 6) which corresponds to an age of 2502±100 Ma that is similar to that of molybdenite. However, K-feldpar and molybdenite define 2 parallel isochrons. This rules out the possibility that the radiogenic Pb component in the KF comes from traces of molybdenite and it suggests that K-feldspar and molybdenite crystallized from parent fluids having different initial Pb isotopic compositions. In addition, the least radiogenic KF from this mineralized pegmatite has a $^{206}Pb/^{204}Pb$ ratio comparable to that determined by Gariépy and Allègre (1985) for KF from the main body of the Preissac intrusion, but a higher $^{207}Pb/^{204}Pb$ ratio. This also suggests that the pegmatite formed from a magmatic source different from that of the main body.

Three analyses were obtained for sample IIPM where molybdenite was hosted in a massive quartz vein. The data plot on the isochron defined by molybdenite from sample IPM (Fig. 2a) indicating that both samples are cogenetic and were derived from Pb sources with similar isotopic compositions.

The Pb isotopic composition of molybdenite from samples IIIPM and IVPM, two granitic pegmatites, are shown in Fig. 2b. The 6 data points appear to fit a single line with a slope of 0.1701±0.0008 (MSWD = 13.8) which would correspond to an age of 2558±28 Ma. The data for samples IIIPM and IVPM are also collinear (MSWD = 11.2) with the results obtained on KF from sample IPM (Fig. 2b). An age of 2589±15 Ma is obtained when the KF data are regressed with the molybdenite data. This age is identical to a Pb-Pb age of 2595±5 Ma defined by molybdenite and K-feldspar from a pegmatite of the Massbéryl prospect in the Lacorne pluton (Carignan and Gariépy 1992).

The $^{238}U/^{204}Pb$ ratio ($\mu$) of the different molybdenite grains can be calculated using the $^{206}Pb/^{204}Pb$ ratio determined for the bulk aliquot and assuming that their initial composition was comparable to that of the least radiogenic K-feldspar. For an age of 2.6 Ga, this yields $\mu$ values of 98 (IPM), 81 (IIPM), 71 (IIIPM) and 109 (IVPM). Aliquots of molybdenite from samples IPM, IIIPM and IVPM were also analyzed for their Pb and U concentrations (Table 2). The molybdenite samples contain between 24 and 40 ppm of common Pb and comparable amounts of radiogenic Pb. However, their U content is very low, ranging from 0.6 to 15.3 ppm; this corresponds to $\mu$ values of 1.1 to 21.0 that are much lower than those inferred above. Accordingly, the three samples plot well above the concordia curve in the $^{206}Pb/^{238}U$ versus $^{207}Pb/^{235}U$ diagram testifying of a massive loss of uranium. Losses of 80 to 99% of the U content initially present in the mineral are required to explain the observed discordancy pattern of these samples. The $^{207}Pb/^{206}Pb$ ages of these samples range from 2.55 to 2.69 Ga (Table 2) but are highly inaccurate because of the large common Pb content of molybdenite and the uncertainties concerning its initial isotopic composition. For example, a difference of 0.5 unit in the value of the initial $^{207}Pb/^{204}Pb$ compositions can change the calculated $^{207}Pb/^{206}Pb$ age by more than 100 Ma.

Figures 2c and 2d show the $^{208}Pb/^{204}Pb$ composition of molybdenite leachates and residues as a function of the $^{206}Pb/^{204}Pb$ ratio. The results for sample IPM are positively correlated in Fig. 2c along a line corresponding to a low Th/U ratio of 0.41±0.03 (MSWD = 9.6). As was the case in Fig. 2a, the regression line for sample IPM does not intersect the initial Pb isotopic composition as defined by the K-feldspar data.

Molybdenite for samples IIPM (Fig. 2c), IIIPM and IVPM (Fig. 2d) yield apparent Th/U ratios of 0.95±0.09, 1.31±0.25 and 1.74±0.25, respectively. In all three cases, the projection of the reference line towards unradiogenic values yields unrealistically low initial $^{208}Pb/^{204}Pb$ ratio for a mineral of late Archean age.

*Cadillac Mine*

Three molybdenite samples and co-existing quartz, K-feldspar or muscovite from the Cadillac Mine were analyzed. As for the Preissac Mine, the molybdenite leachates and residues have a wide range of Pb-isotopic compositions (Table 1) with $^{206}Pb/^{204}Pb$ ratios varying from 25 to 101.

Results for molybdenite from a massive quartz vein (sample ICM) are positively correlated in a $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (Fig. 3a) and the slope of 0.1464±0.0012 (MSWD = 4.4) corresponds to an age of 2304±16 Ma. The data for a quartz leachate and a residue define a line of similar slope but slightly displaced above the molybdenite isochron.

The results for molybdenite and KF from a granitic pegmatite (sample IICM) are shown in Fig. 4a. All data points are collinear defining a line with a slope of 0.1701±0.0023 (MSWD = 0.8) that corresponds to an age of 2560±20 Ma. The composition of the KF residue is identical to that determined for the main body of the Preissac granite (Gariépy and Allègre 1985).

The results obtained on molybdenite from sample IIICM, a massive quartz vein, are all very radiogenic (Table 1) but not correlated in the $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (Fig. 4b), although they grossly plot on the extension of the isochron defined for sample IICM. A sample of muscovite from IIICM also plots close to that line.

The calculated $\mu$ values assuming and age of 2.6 Ga, and using the composition of the bulk molybdenite aliquots and that of the K-feldspar residue are, 103 (ICM), 17 (IICM) and 169 (IIICM). The measured U content of molybdenite from samples ICM and IIICM are 10.5 and 42.26 ppm, and the $\mu$ values 51.6 and 98.5, respectively. These two samples have also suffered important U-losses in the range of 35 to 45% of the initial content.

The results for molybdenite from sample ICM are positively correlated in the $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (Fig. 3b) along a line corresponding (MSWD = 12.4) a Th/U ratio of 0.98±0.03, but the data for molybdenite from samples IICM and IIICM are not.

*Heigh of Land deposit*

Molybdenite from a quartz-muscovite vein of the Heigh of Land deposit has yielded a narrower range of Pb-isotopic compositions with $^{206}Pb/^{204}Pb$ ratios varying from 39.3 to 48.5 (Table 1). The results are positively correlated in the $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (Fig. 5a) and define a line with a slope of 0.1069±0.0040 (MSWD = 1.3) that corresponds to an age of 1748±72 Ma. Impure vein muscovite with small inclusions of molybdenite was also analyzed. Two leachates of muscovite done with concentrated HCl and $HNO_3$ have yielded very radiogenic compositions while the residue has much lower Pb isotopic compositions (Fig. 5a). The slope of the line defined by these 3 points would correspond to an age of 2818±30 Ma which is older than any dated rocks in the area. Even if care was taken to remove the molybdenite inclusions before analysis, the distribution of the data more likely reflects simple mixing between the two mineral phases and therefore has no age significance. However, the low $^{207}Pb/^{204}Pb$ ratio of the residue indicate that the crystallization age of the mica is late Archean. The Heigh of Land molybdenite has U and common Pb contents of 6.1 and 253 ppm, respectively (Table 2). As was the case for the other deposits, this corresponds to a very low present-day $\mu$ value of 2.5.

The results for this molybdenite are also well correlated in the $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (MSWD = 1.7; Fig. 5b) with a slope corresponding to a Th/U ratio of 1.58±0.04. As was the case for three samples from the Preissac Mine, the projection of the regression line towards unradiogenic values yields an unrealistically low initial $^{208}Pb/^{204}Pb$ ratio.

*La Pause deposit*

The La Pause molybdenite yielded a very narrow range of Pb isotopic compositions with $^{206}Pb/^{204}Pb$ ratios varying only from 13.5 to 15.0 (Table 1). In Fig. 6, the data points are parallel to a 2.6 Ga reference isochron suggesting that the ore has an age similar to the other Mo deposits in the area. The $^{206}Pb/^{204}Pb$ ratio of residue R1, which was analyzed after the sample was leached twice (Table 1) is even comparable to that of K-feldspar from late granitoid intrusives in the area (Gariépy and Allègre 1985; Carignan et al. 1992a). The subsequent leachate (L3) was more radiogenic, but there was unfortunately insufficient Pb remaining in the final residue to measure its isotopic composition adequately.

Unradiogenic molybdenite from the Hemlo Au-Mo deposit in the Hemlo-Heron Bay greenstone belt, west of the Abitibi belt, has also been reported by Thorpe (1986) and Corfu and Muir (1989). At this locality, the ore is contained in medium grade metamorphic rocks and its formation may be related to metamorphism and late hydrothermal activity between 2680 Ma and 2670 Ma (Corfu and Muir 1989). Molybdenite, K-feldspar, and other Pb-rich phases related to the mineralization have yielded homogeneous low $^{207}Pb/^{204}Pb$ ratios of *ca.* 14.5, suggesting that magmas and fluids were derived from juvenile crust without the involvement of older mature crustal materials (Corfu and Muir 1989). The higher $^{207}Pb/^{204}Pb$ ratio of the La Pause molybdenite (14.6) compared to that of U-poor sulfides from komatiite lava flows (*ca* . 14.4; Brévart et al. 1986) and to that of the Hemlo deposit suggests that the mineralized fluid dissolved a significant amount of crustal Pb. This Pb may come from the radiogenic late K-rich plutons of the Preissac-Lacorne-LaMotte block and/or from the surrounding sediments.

*Massberyl prospect*

A bulk aliquot of molybdenite from a muscovite-garnet-K-feldspar-spodumene dyke in the northern part of the Lacorne pluton has yielded a $^{206}Pb/^{204}Pb$ ratio of 127.3 and a Pb-Pb isochron age of 2.6 Ga (Carignan and Gariépy 1992). The $^{238}U/^{204}Pb$ ratio of this molybdenite should thus exceed a value of 220, but the measured ratio is equal to a very low value of 0.15 which indicates a uranium loss larger than 99%.

## Discussion

The new results obtained for molybdenite deposits of the Preissac-Lacorne-Lamotte intrusive complex raise several questions which will be addressed below. These questions are: What are the causes and consequences of the important uranium deficiency observed in all analyzed molybdenites? What is the geological significance of the young ages observed in samples HL, ICM and IPM? Why do molybdenite samples from the same deposit record different Pb-Pb ages and Th/U ratios?

*Uranium loss*

Molybdenite systematically has an important deficit of uranium and this deficit is highly variable in magnitude, even at the scale of a given deposit. In the samples studied here, the deficit has been estimated to vary from about 35% in a sample from the Cadillac Mine to more than 99% in the Masbéryl prospect. One puzzling observation is that, contrary to most other U-bearing minerals, the parent isotopes instead of the daughter products leave the mineral. In addition, the Re-Os isotopic system appears to display the same behaviour in molybdenite (Luck and Allègre 1982). In the case of the Re-Os isotopic system, this was even more unexpected because barely any common Os is present in molybdenite, suggesting to a first approximation that this element is not accepted in molybdenite during the crystallization.

Uranium and rhenium thus appear to be very weakly bound in molybdenite. This may relate to the layer structure of the mineral where the bond strengths within the individual $MoS_2$ layers are much stronger than between the layers and speculate that part or all of the U and Re atoms are located along the {0001} cleavage planes. This raises the question whether uranium (or rhenium) is continuously or only episodically lost from the mineral.

Figure 7 shows the results of calculations that were made assuming that uranium was continuously lost from a molybdenite initially formed at 2.65 Ga with a $^{238}U/^{204}Pb$ ratio of 100 and initial Pb isotopic compositions typical of late-tectonic K-rich granites of the Abitibi belt. The diagram shows the apparent present day Pb-Pb age resulting from the loss as a function of the total U lost since crystallization. The diagram shows that any loss of U should increase the apparent Pb-Pb ages. For example, a continuous U-loss resulting in a total deficit of 40% for this element will yield an apparent Pb-Pb age greater than 2.75 Ga (Fig. 7). For total uranium deficits exceeding 80%, the apparent ages will be greater than 2.9 Ga (Fig. 7). This can only indicate that U-loss is largely a recent phenomenon. This is strengthened by the lack of any correlation between the total uranium deficits and the apparent Pb-Pb ages.

The hypothesis that molybdenite did not loose uranium but gained labile radiogenic Pb released from U-rich minerals is ruled out. If that was the case, molybdenite Pb-Pb isochrons should yield the same age as the host rocks. In addition, the calculated Th/U ratio of molybdenite, which only depends on the amount of $^{208}$Pb present in the mineral, should be comparable to that of crust forming silicate rocks *i.e.* generally higher than 3.5 (Faure 1986).

The cause of recent uranium departure in highly variable amounts is most likely related to the redox state of this element. In molybdenite, uraniume likely occurs as the U(IV) species as is the case for molybdenum. However, under oxidizing conditions uranium forms the highly soluble U(VI) species (Langmuir 1978). Similarly, Re has been detected in all valence state from -1 to +7 but +4 and +7 are the most important geologically (Shirey 1991). Circulation of meteoric water inducing changes in the pH and redox conditions towards an oxidizing environment could explain the recent departure of uranium and possibly of Re. This interpretation is also compatible with the observation that highly variable U deficits reflect the local hydraulic conditions which highly influence the circulation of meteoric water. This might even have been enhanced in some samples by the mining activities themselves. Because of its geochemical properties, some Pb should also be dissolved in oxidized meteoric fluids but to a lesser extent than uranium (Gariépy and Dupré 1991).

*Geological significance of the Pb-Pb ages*

Samples HL, ICM and IPM have yielded young molybdenite Pb-Pb ages of *ca.* 1.8, 2.3 and 2.5 Ga, respectively. In the case of samples IPM and HL, the distribution of the results in the $^{207}$Pb/$^{204}$Pb versus $^{206}$Pb/$^{204}$Pb diagrams (Figs. 2a and 5a) is analogous to the pattern observed for molybdenite of the Pidgeon Molybdenum Mine in the Wabigoon Subprovince (Carignan and Gariépy 1992): the projection of the molybdenite isochrons towards unradiogenic values passes significantly above the initial Pb isotopic composition as defined by the data obtained on the K-feldspar. Carignan and Gariépy (1992) suggested that this is due to younger thermal resetting of molybdenite and concomitant homogeneization of all Pb present in the mineral. These authors also presented a method allowing to estimate the bulk Pb isotopic compositions of molybdenite at the time of thermal reset and to deduce the value of the U/Pb and Th/U ratios before and after this event.

Assuming that the Heigh of Land deposit formed at 2.64 Ga (the age of the host Lamotte pluton; Machado et al. 1992), with initial Pb isotopic compositions similar to the main granite body and that it was thermally reset at 1.75 Ga requires that the $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios of the bulk molybdenite at the time of the event were 30.3 and 19.5, respectively. From this result, one can calculate that the $^{238}U/^{204}Pb$ ratios of molybdenite before and after the thermal event were ~80 and 55, respectively. Thus molybdenite appears to have lost ~33% of its uranium during the crisis, a figure that is very similar to that obtained for the Pidgeon Molybdenum deposit (Carignan and Gariépy 1992). In the case of the IPM sample from the Preissac Mine, the values of the $^{238}U/^{204}Pb$ ratio of molybdenite before and after the event are estimated at ~160 and 90, respectively, and correspond to a U-loss of ~40%. However, note that in this deposit, the thermal resetting event (2.49 Ga) is close to the assumed mineralization age (2.64 Ga); in such a case, the calculations are very sensitive to the choices made for the ages of the events and for the initial Pb isotopic compositions.

The apparent Th/U ratio of molybdenite from the Heigh of Land deposit is 1.58 (Fig. 5b) and the projection of the line towards unradiogenic values points towards an unrealistically low initial $^{208}Pb/^{204}Pb$ value. Assuming that molybdenite indeed has a Th/U ratio of 1.58 and using the value of 30.3 calculated above for the initial $^{206}Pb/^{204}Pb$ composition at 1.75 Ga, its $^{208}Pb/^{204}Pb$ ratio at 1.75 Ga is estimated to be ~36.0. If molybdenite evolved from an initial composition similar to that of K-feldspar from the main granite body, then its Th/U ratio during the 2.64-1.75 Ga time interval was ~0.7, a value that is comparable to that of several molybdenite deposit that do not seem to have been perturbed (Deloule et al. 1989; Carignan and Gariépy 1992). Thus alignments in the $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ which point towards unrealistically low initial $^{208}Pb/^{204}Pb$ ratios, as is the case for molybdenite samples IIPM, IIIPM and IVPM (Figs. 2c,d) most likely reflect secondary perturbations inducing U-loss. One exception has to be made for sample IPM where the Th/U ratio does not appear to have changed much before and after the perturbation. However, the uncertainties concerning the ages of deposition and the perturbation are too large to confirm this observation.

Figure 8 shows the Pb-Pb molybdenite ages determined in this study in comparison to the age of the volcano-plutonic activity in the southern Abitibi belt and to the age of late- to post-Archean tectono-magmatic events known to have taken place in the Superior Province. These events are: 1) the deposition and/or the remobilization of lode Au-deposits along the Cadillac-Larder Lake fault zone (Hanes et al. 1989; Anglin 1990; Jemielita et al. 1990; Schandl et al. 1990; Corfu and Davis 1991; Wong et al. 1991; Claoué-Long et al. 1992); 2) the intrusion of the Matachewan dykes dated with the Pb-Pb isochron method at 2480±34 Ma (Smith and Farquhar 1988) and at 2454+3/-2 by the U-Pb concordia method (Heaman 1989); 3) the intrusion of Early Proterozoic dyke swarms (Preissac, Fort Frances and Nipissing dykes) that occurred between between 2.1 and 2.3 Ga (Corfu and Andrews 1986; Anglin 1990; Buchan et al. 1991); 4) the reactivation of Archean major faults in the western Superior Province dated by the Rb-Sr method on pseudotachylite at 1.95 Ga (Peterman and Day 1989); and 5) the regional alteration of the Proterozoic Abitibi dykes that took place between 1.8 Ga and 1.7 Ga (Hanes and York 1979).

The Pb-Pb ages determined for molybdenite correspond exactly to four of these tectono-magmatic events (Fig. 8) a coincidence that is unlikely to be fortuitous. The ages of samples IPM and ICM correspond exactly to the emplacement age of the Matachewan and the early Protorezoic dykes, respectively, and the age obtained for the Heigh of Land deposit is similar to the period of alteration of the Proterozoic Abitibi dykes. The Proterozoic Pb-Pb ages recorded by molybdenite in the Preissac-Lacorne-Lamotte intrusive complex are thus interpreted to reflect a thermal perturbations of the isotopic system during dyke emplacement or alteration. Proterozoic remobilizations in the range of 2.15 Ga to 2.25 Ga of sulfides from Pb and Ni-Cu deposits have also been reported for the late Archean Baby-Belleterre greenstone belt of the Pontiac Subprovince (Carignan et al. 1992b).

The oldest molybdenite group (2.56 to 2.60 Ga) may be related to the same hydrothermal event like inferred to be responsible for the deposition or the remobilization of lode Au along the Cadillac-Larder Lake fault zone. Actually, the association Au and Mo is not unusual (Cameron and Hattori 1985; Jébrak 1992, Jébrak and Harnois 1991): the precipitation temperatures of the two elements as determined from fluid inclusion studies are comparable (350-450°C) and $CO_2$ rich fluid inclusions are found in both deposit types (Mulja et al. 1990; Brown and Lamb 1986).

In contrast to the lode Au deposits, the pegmatite hosted molybdenite ores are clearly orthomagmatic and should thus be 2.64 Ga old or more. This raises the question whether the Pb-Pb isochrons record 1) cooling below a given isotherm or 2) younger discrete thermal pulses. There are three lines of evidence favoring the hypothesis of discrete thermal pulses. Firstly, it better explains the age differences observed in molybdenite samples from the same deposit. Thermal pulses would induce fluid circulation along fractures and faults, and the proximity of a particular molybdenite to such structures will influence its apparent age. Secondly, we have shown that steep alignments in the $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram with unrealistically low initial $^{208}Pb/^{204}Pb$ ratios are best explained by important episodic U-loss. Samples IIPM, IIIPM and IVPM from the Preissac deposit do show this feature (Figs. 2c,d). Finally, this would be compatible with the presence of a second generation of low temperature and low salinity fluid inclusions in these deposits (Mulja et al. 1990).

## Conclusions

The investigation of molybdenite deposits from the Preissac-Lacorne-Lamotte intrusive complex with the U-Pb isotopic system shows that:

1) in most cases, molybdenite has very radiogenic compositions leading to (using a differential dissolution technique) a large enough spread of analytical results on a Pb-Pb isochron diagram to define meaningful ages;
2) molybdenite ages in the range of 2.56 to 2.60 Ga can be related to regional thermal pulses affecting the late Archean Abitibi greenstone belt well after the termination of the

magmatic cycles;

3) molybdenite ages of *ca.* 2.5, 2.3 and 1.75 Ga are related to punctual thermal perturbations corresponding respectively to the intrusion of the Matachewan and Preissac-Nipissing dykes, and to the alteration of the Proterozoic Abitibi dykes;

4) molybdenite always has important and variable deficits of uranium compared to Pb, reaching values > 99% and, as a direct consequence, cannot be dated with the U-Pb method;

5) the uranium deficiencies are best explained by recent loss of U in response to changes in the redox and pH conditions induced by meteoric water circulation.

## Acknowledgments

This study was supported by a research agreement from Energy, Mines and Resources Canada and by operating grants (CG, NM) and post-graduate scholarships (JC) from the Natural Sciences and Engineering Council (NSERC) of Canada and from the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (FCAR) of Québec. Laboratory costs at GEOTOP are partially supported by infrastructure grants from NSERC and FCAR.

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## Figure captions

Fig. 1. Geological map of the south-central Abitibi Subprovince showing the location of the studied molybdenum deposits; modified from Rive et al. (1990) and Jébrak (1992).

Fig. 2. Pb isotopic results for the Preissac deposit shown in $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagrams and in $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram. Filled symbols = molybdenite; open symbols = K-feldspar; circles = sample IPM; diamonds = sample IIPM; triangles = sample IIIPM; squares = sample IVPM.

Fig. 3. a) $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram and b) $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram showing the results obtained on sample ICM from the Cadillac Mine. Filled circles = molybdenite; open triangles = quartz.

Fig. 4. $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagrams showing the Pb isotopic results for the a) IICM and b) IIICM samples. Filled circles = IICM molybdenite; open squares = IICM K-feldspar; filled diamonds = IIICM molybdenite; open diamonds = IIICM mica.

Fig. 5. Pb isotopic results for the Heigh of Land deposit shown in a) $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ and b) $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagrams. Circles = molybdenite; squares = mica. The line through the mica results represents a mixing line between mica and molybdenite.

Fig. 6. Pb isotopic results for the La Pause deposit shown in a $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram. The compositional domains of the mantle and the ancient crust reservoir in the Abitibi belt (Gariépy and Allègre 1985; Deloule et al. 1989; Carignan et al. 1992a) and a 2.6 Ga reference isochron are shown for comparison.

Fig. 7. Diagram showing the calculated apparent Pb-Pb ages resulting from a continuous

departure of U from molybdenite as a function of the total U lost since crystallization. The calculations were made for a 2.65 Ga old molybdenite having a $^{238}U/^{204}Pb$ ratio of 100 and initial $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios of 13.7 and 14.65, respectively.

Fig. 8. Diagram showing the Pb-Pb molybdenite ages determined in this study, with their two $\sigma$ error bars, compared to that of tectono-magmatic events known to have taken place in the southern Abitibi greenstone belt.

Table 1. Pb-isotopic compositions of molybdenite and associated minerals.

| Sample | | $^{206}Pb/^{204}Pb$ | $^{207}Pb/^{204}Pb$ | $^{208}Pb/^{204}Pb$ |
|---|---|---|---|---|
| **Preissac Molybdenum Mine** | | | | |
| IPM | B | 62.464 | 23.903 | 39.756 |
| | L1 | 64.086 | 24.166 | 39.826 |
| | L2 | 60.782 | 23.862 | 39.103 |
| | R1 | 40.535 | 20.442 | 37.024 |
| | L3 | 48.446 | 21.535 | 38.407 |
| | R2 | 40.548 | 20.382 | 36.978 |
| IPM - KF. 1 | L1 | 21.129 | 15.949 | 34.310 |
| | R1 | 14.858 | 14.972 | 33.580 |
| IPM - KF. 2 | L1 | 14.241 | 14.859 | 33.621 |
| | R1 | 13.807 | 14.682 | 33.349 |
| IIPM | B | 53.836 | 22.236 | 40.096 |
| | L1 | 54.114 | 22.610 | 39.842 |
| | R | 42.554 | 20.794 | 36.942 |
| IIIPM | B | 49.286 | 20.863 | 44.931 |
| | L1 | 63.521 | 23.265 | 49.439 |
| | R1 | 30.306 | 17.739 | 37.488 |
| IVPM | B | 68.033 | 24.157 | 48.617 |
| | L1 | 74.943 | 25.267 | 51.410 |
| | R1 | 64.133 | 23.671 | 46.095 |
| **Cadillac Molybdenum Mine** | | | | |
| ICM | B | 65.543 | 22.285 | 48.302 |
| | L1 | 60.877 | 21.253 | 47.146 |
| | L2 | 56.004 | 20.917 | 46.033 |
| | R1 | 51.749 | 20.376 | 44.513 |
| | L3 | 31.305 | 17.357 | 39.525 |
| | L4 | 22.066 | 15.892 | 36.119 |
| | R2 | 24.649 | 16.300 | 37.258 |
| ICM - Quartz | L1 | 26.434 | 16.841 | 38.017 |
| | R1 | 18.606 | 15.740 | 33.792 |
| IICM | B | 22.249 | 16.090 | 37.717 |
| | L1 | 24.180 | 16.358 | 38.296 |
| | R1 | 25.379 | 16.609 | 36.728 |
| IICM - KF | L1 | 13.892 | 14.654 | 33.567 |
| | R1 | 13.529 | 14.574 | 33.221 |
| IIICM | B | 97.971 | 30.316 | 75.017 |
| | L1 | 101.167 | 29.142 | 77.653 |
| | R1 | 87.114 | 29.102 | 68.522 |
| IIICM - mica | B | 38.876 | 18.228 | 44.364 |

Table 1. Pb-isotopic compositions of molybdenite and associated minerals (continued).

| Sample | | $^{206}Pb/^{204}Pb$ | $^{207}Pb/^{204}Pb$ | $^{208}Pb/^{204}Pb$ |
|---|---|---|---|---|
| **Heigh of Land deposit** | | | | |
| HL | B | 47.302 | 21.397 | 44.006 |
| | L1 | 48.541 | 21.504 | 44.580 |
| | L2 | 48.019 | 21.367 | 44.589 |
| | R1 | 39.338 | 20.486 | 40.497 |
| | L3 | 43.883 | 21.010 | 42.465 |
| | R2 | 39.500 | 20.525 | 40.474 |
| HL - mica | L1 | 42.813 | 20.170 | 43.152 |
| | L2 | 41.924 | 19.867 | 42.657 |
| | R1 | 16.712 | 14.913 | 34.117 |
| **La Pause deposit** | | | | |
| LP | B | 13.689 | 14.702 | 33.785 |
| | L1 | 14.564 | 14.854 | 34.164 |
| | L2 | 14.622 | 14.827 | 34.306 |
| | R1 | 13.522 | 14.605 | 33.444 |
| | L3 | 14.971 | 14.875 | 34.371 |

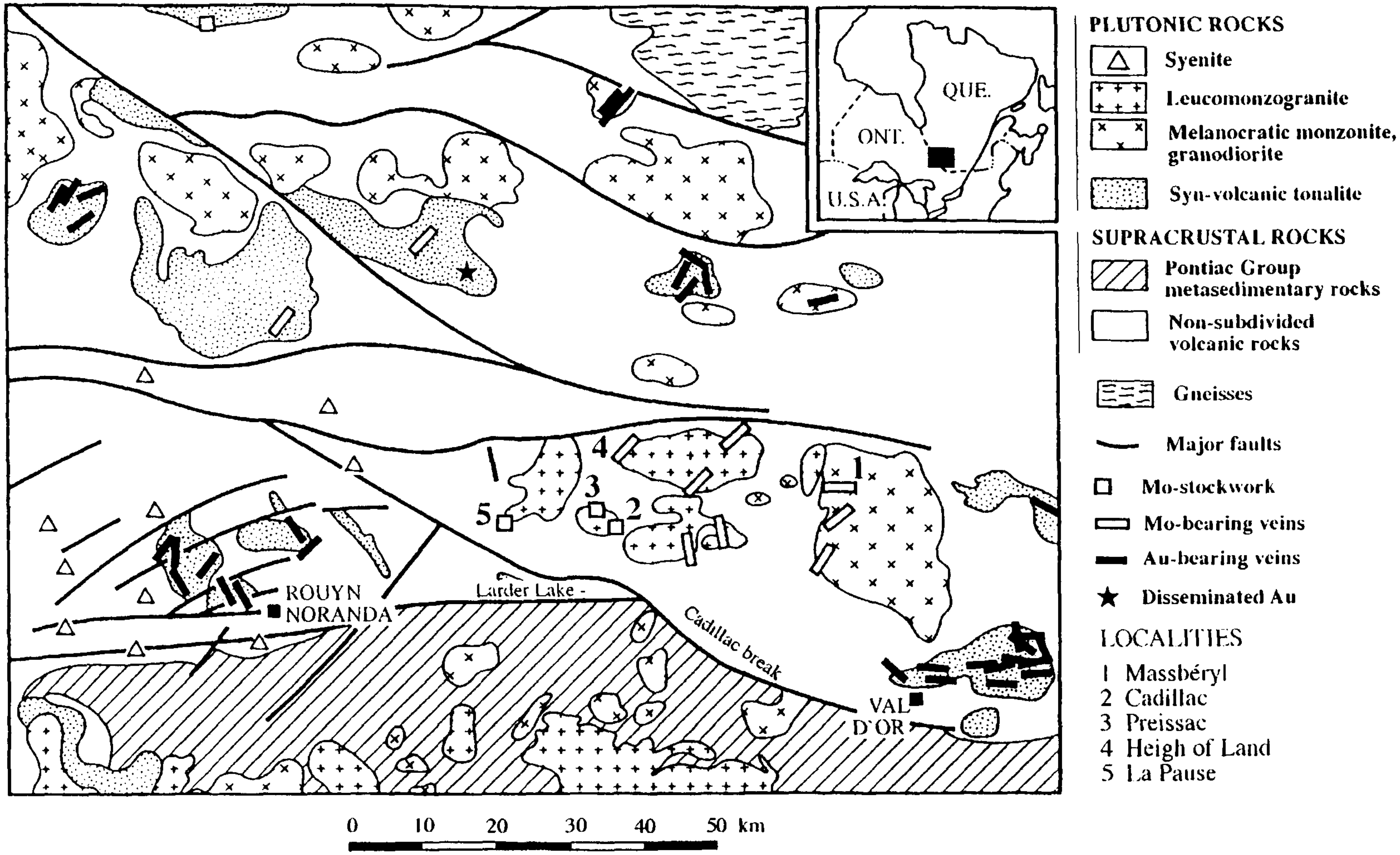
B: bulk; L: leachate; R residue

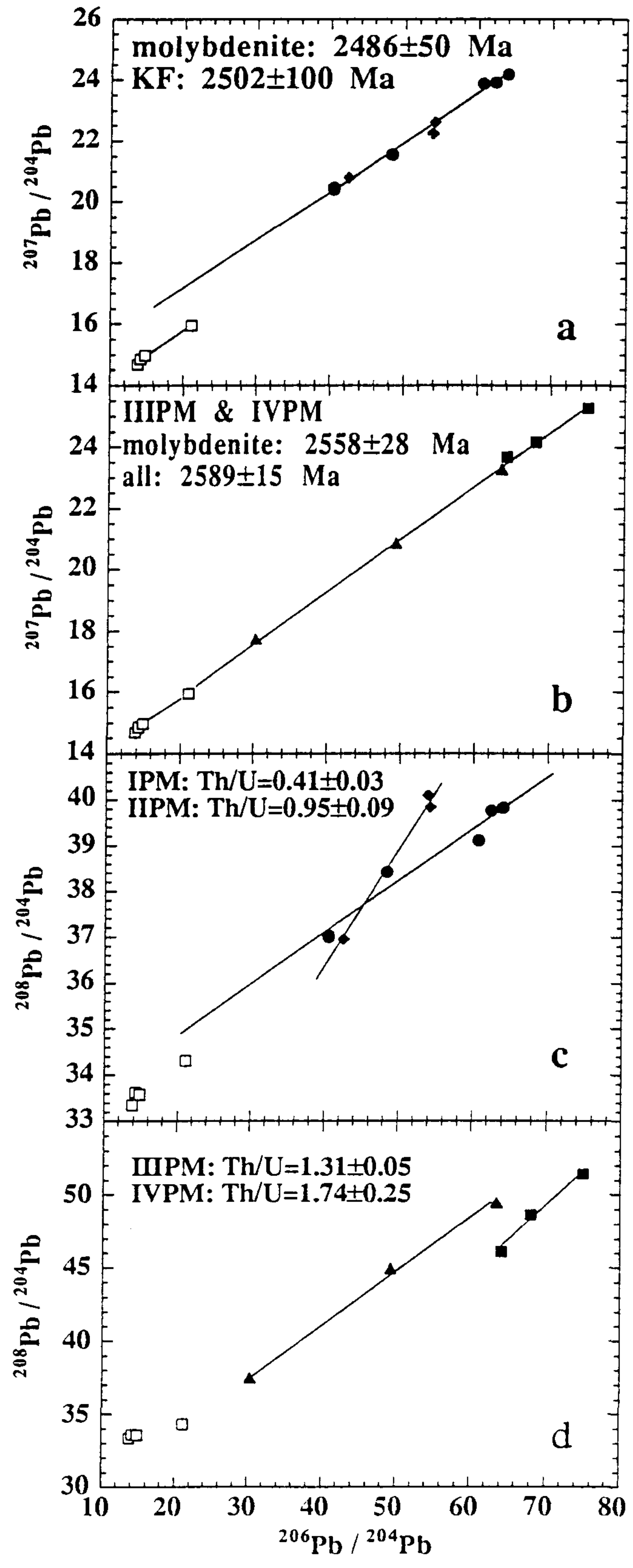
Table 2. U-Pb results for molybdenite

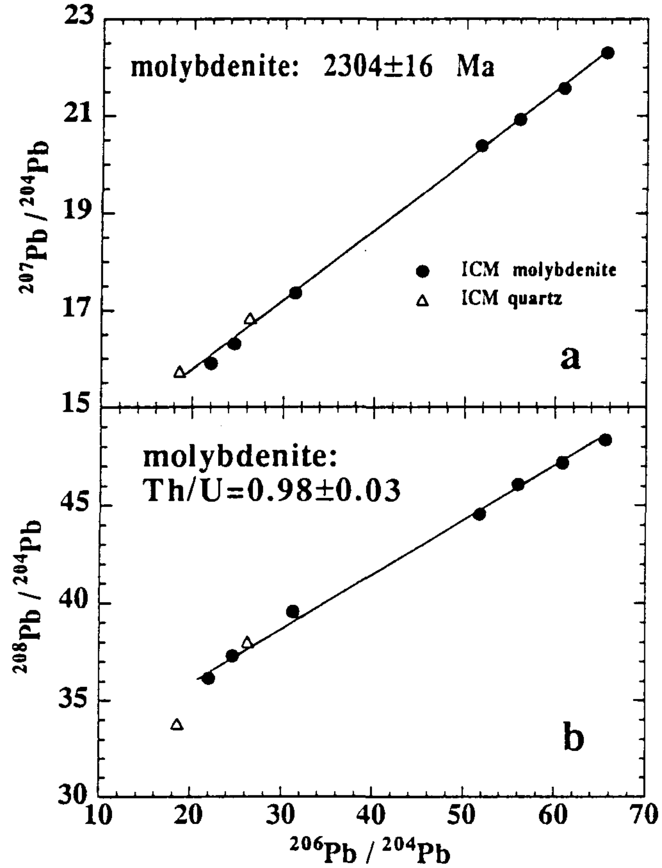
| Sample | weight (mg) | concentrations (ppm) | | | atomic ratios[1] | | | | age (Ma) |
|---|---|---|---|---|---|---|---|---|---|
| | | U | $Pb_c$ | $Pb_r$ | $^{238}U/^{204}Pb$ | $^{206}Pb/^{238}U$ | $^{207}Pb/^{235}U$ | $^{207}Pb/^{206}Pb$ | $^{207}Pb/^{206}Pb$ |
| IPM | 0.91 | 4.09 | 24.06 | 23.50 | 9.29 | 5.0779 | 128.466 | 0.1835 | 2685 |
| IIIPM | 4.68 | 0.64 | 31.05 | 32.99 | 1.13 | 40.315 | 940.393 | 0.1692 | 2550 |
| IVPM | 4.40 | 15.25 | 39.70 | 48.93 | 21.00 | 2.5878 | 61.0925 | 0.1712 | 2570 |
| ICM | 1.14 | 10.54 | 11.52 | 9.58 | 51.62 | 0.7523 | 14.5978 | 0.1407 | 2236 |
| IIICM | 2.64 | 42.26 | 24.72 | 53.23 | 98.45 | 0.8725 | 20.4698 | 0.1702 | 2560 |
| HL | 0.82 | 6.13 | 130.98 | 122.18 | 2.53 | 15.361 | 409.263 | 0.1932 | 2770 |
| HL[2] | 0.82 | 6.13 | 182.48 | 70.68 | 2.53 | 8.7333 | 142.419 | 0.1183 | 1930 |
| MB | 0.23 | 0.28 | 99.58 | 247.77 | 0.15 | 710.71 | 16963.1 | 0.1731 | 2588 |

[1]corrected for spike, blank, and common Pb using Stacey and Kramers's (1975) two-stage growth curve.
$Pb_c$ = total common Pb; $Pb_r$ = radiogenic Pb.

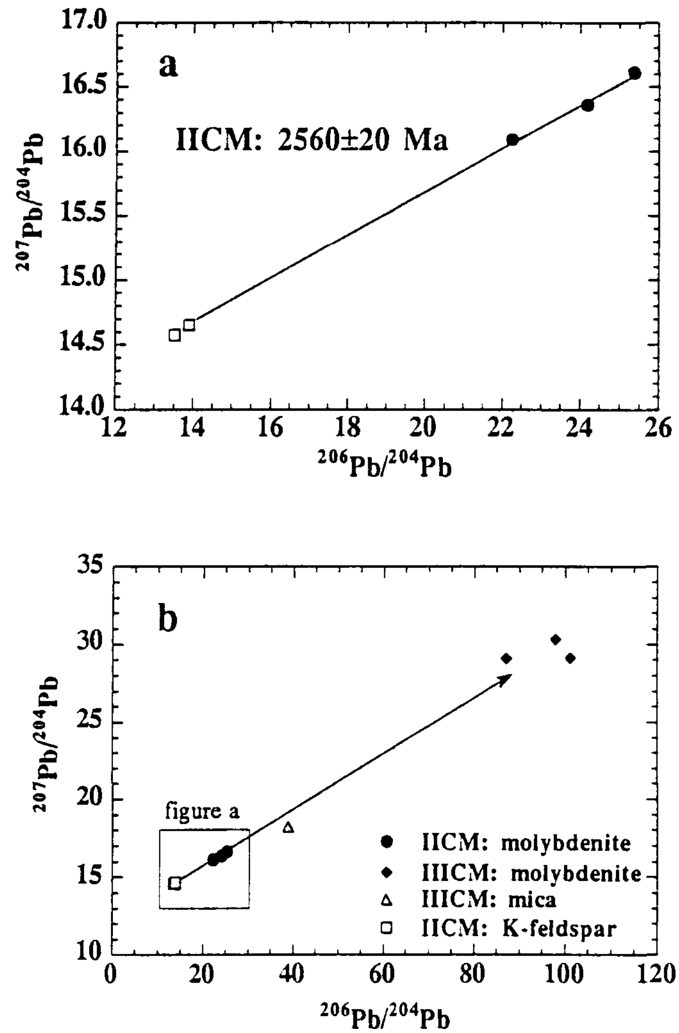
[2]corrected using initial Pb isotopic compositions discussed in text.

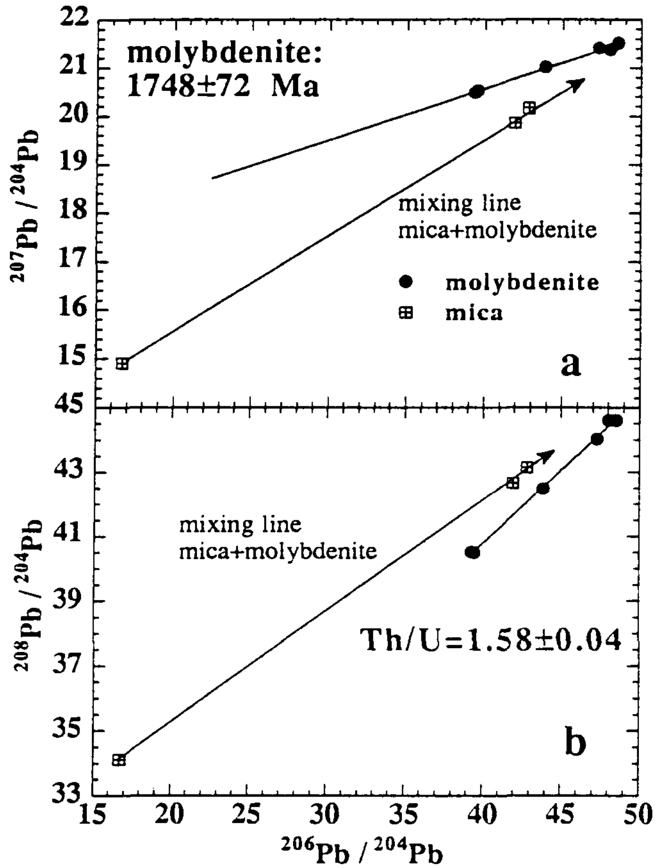

QUE.
ONT.
U.S.A.
ROUYN
NORANDA
Larder Lake -
Cadillac break
VAL
D'OR
1
2
3
4
5
0 10 20 30 40 50 km
PLUTONIC ROCKS
Syenite
Leucomonzogranite
Melanocratic monzonite, granodiorite
Syn-volcanic tonalite
SUPRACRUSTAL ROCKS
Pontiac Group metasedimentary rocks
Non-subdivided volcanic rocks
Gneisses
Major faults
Mo-stockwork
Mo-bearing veins
Au-bearing veins
Disseminated Au
LOCALITIES
1 Massbéryl
2 Cadillac
3 Preissac
4 Heigh of Land
5 La Pause


molybdenite: 2486±50 Ma
KF: 2502±100 Ma
a
IIIPM & IVPM
molybdenite: 2558±28 Ma
all: 2589±15 Ma
b
IPM: Th/U=0.41±0.03
IIPM: Th/U=0.95±0.09
c
IIIPM: Th/U=1.31±0.05
IVPM: Th/U=1.74±0.25
d
207Pb / 204Pb
208Pb / 204Pb
206Pb / 204Pb

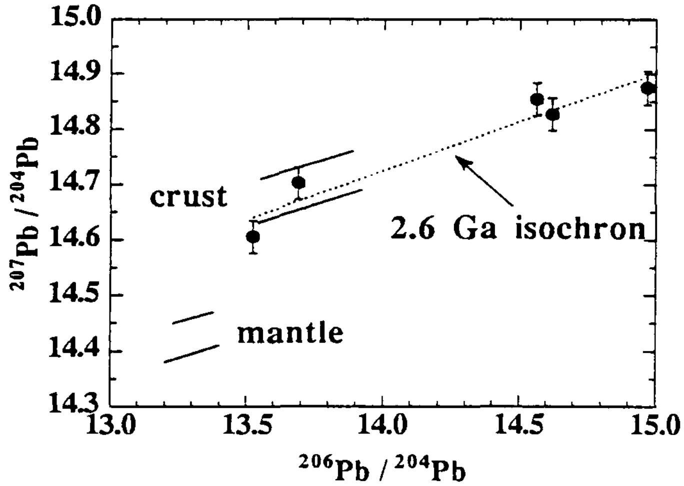


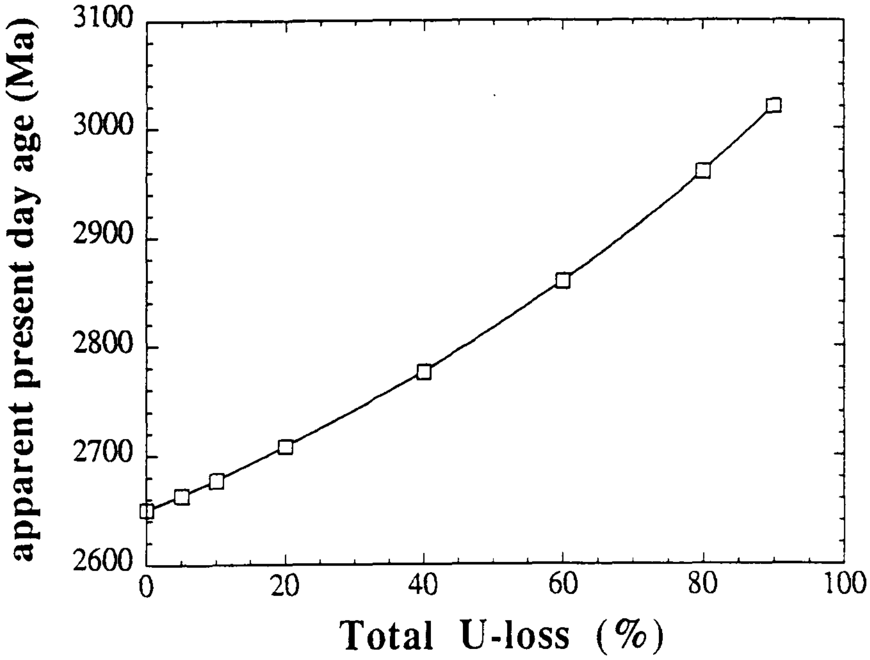
molybdenite: 2304±16 Ma
ICM molybdenite
ICM quartz
a
molybdenite:
Th/U=0.98±0.03
b
207Pb / 204Pb
208Pb / 204Pb
206Pb / 204Pb
23
21
19
17
15
45
40
35
30
10
20
30
40
50
60
70

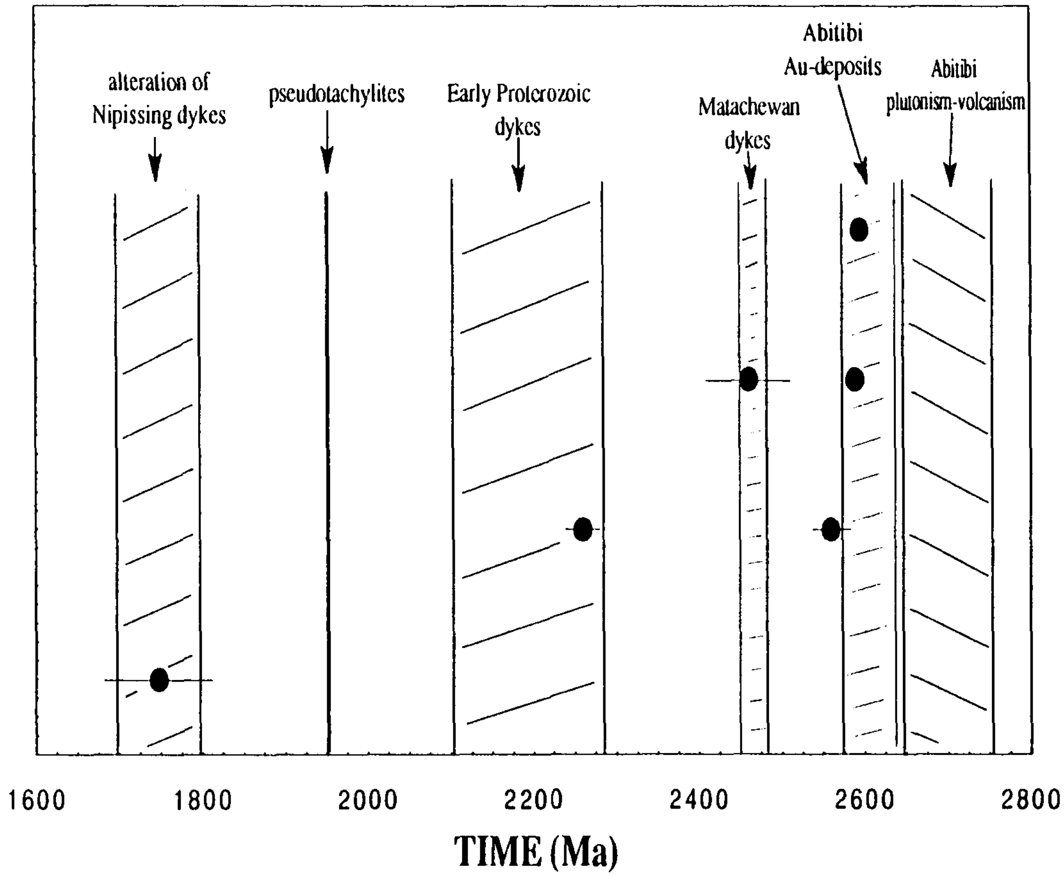

a
IICM: 2560±20 Ma
$^{207}Pb/^{204}Pb$
$^{206}Pb/^{204}Pb$
b
figure a
IICM: molybdenite
IIICM: molybdenite
IIICM: mica
IICM: K-feldspar
$^{207}Pb/^{204}Pb$
$^{206}Pb/^{204}Pb$



molybdenite:
1748±72 Ma
mixing line
mica+molybdenite
molybdenite
mica
a
mixing line
mica+molybdenite
Th/U=1.58±0.04
b
207Pb / 204Pb
208Pb / 204Pb
206Pb / 204Pb


15.0
14.9
14.8
14.7
14.6
14.5
14.4
14.3
13.0
13.5
14.0
14.5
15.0
207Pb / 204Pb
206Pb / 204Pb
crust
mantle
2.6 Ga isochron


apparent present day age (Ma)
3100
3000
2900
2800
2700
2600
0
20
40
60
80
100
Total U-loss (%)



Abitibi
Au-deposits
Abitibi
plutonism-volcanism
alteration of
Nipissing dykes
pseudotachylites
Early Proterozoic
dykes
Matachewan
dykes
1600
1800
2000
2200
2400
2600
2800
TIME (Ma)

# Pb isotope geochemistry of the Silidor and Launay gold deposits, Abitibi Subprovince: Implications for the source of Archean Au

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Submitted for publication to: *Economic Geology*

# INTRODUCTION

Geochronological studies of gold ores in the Abitibi Subprovince of the Canadian Shield have shown that it is feasible to date very precisely, with the U-Pb concordia method, accessory minerals found in the alteration zones of the deposits (Corfu and Muir, 1989; Jemielita et al., 1990; Schandl et al., 1990; Wong et al., 1991). However, minerals such as zircon, monazite, titanite and rutile which are thougth to have precipitated contemporaneously with the ore, have yielded significantly different ages ranging from 2680 Ma for zircon (Claoué-Long et al., 1990, 1992) to 2600 Ma for rutile (Wong et al., 1991). It is noteworthy that these "mineralization ages" are younger than that of the host rocks which yielded ages in the range of 2720 Ma to 2690 Ma (Corfu and Muir, 1989; Wong et al., 1991; Mortensen, 1992a, b). Ar-Ar and Sm-Nd geochronological studies of hydrothermal minerals associated with these gold deposits yielded ages close to rutile U-Pb ages, varying between 2600 Ma and 2550 Ma (Kerrich et al., 1987; Hanes et al., 1989; Anglin, 1990). However, it is not known if the younger ages represent remobilization of the ores and rejuvenation of the isotopic systems (Claoué-Long et al., 1992) or the primary age of mineralization.

Knowledge of the exact timing of Au deposition could significantly help to select between the different models explaining the origin of Archean auriferous fluids. Three mechanisms are frequently invoked: (1) the magmatic model proposes that in some deposits, Au is derived from the same magmatic sources as the host felsic intrusions (*e.g.* Cameron and Hattori, 1987; Burrows and Spooner, 1989); Alternatively, (2) Groves and Phillips (1987) proposed that the mineralizing fluids are generated by prograde metamorphism in the deeper portion of the supracrustal assemblages; lastly, (3) formation of auriferous fluids has been related to deep crustal processes, including outgassing of $CO_2$ from the mantle, granulitization and migmatitization of the lower crust (Cameron, 1988; Colvine et al. 1988; Fyon et al., 1989; Perring et al., 1989).

Carignan et al. (1992) showed that the initial Pb isotopic compositions of the volcanic supracrustal assemblages (2720-2690 Ma), the syn- to late-kinematic granitoids (2720-2680 Ma) and the post-tectonic granitoids (2680-2640 Ma) of the Abitibi greenstone belt are clearly distinguishable from one another. Thus, it should be possible using Pb isotopes to unravel the source reservoir of Au in those deposits where the initial Pb isotopic composition of the ore can be determined accurately.

This study focuses on both U-free and U-bearing minerals from the Silidor Mine and the Launay prospect, two granitoid hosted Au deposits of the Abitibi Subprovince of the Canadian Shield. Its purposes are to identify the source of the mineralization and to define Pb-Pb mineral isochrons yielding absolute ages that are not model-dependent.

## GEOLOGICAL OUTLINE AND SAMPLING

The Abitibi Subprovince is a volcano-plutonic terrane as defined by Card and Cieselski (1986) consisting of metavolcanic rocks, lesser amounts of metasedimentary rocks and abundant igneous intrusions (Ludden at al., 1986; Corfu et al., 1989; Rive et al., 1990; Jackson et al., 1991). Metamorphism is generally below greenschist facies (Jolly, 1978). The volcanic activity occurred between 2.75 and 2.70 Ga while intrusive rocks were mostly emplaced between 2.72 and 2.68 Ga (Frarey and Krogh, 1986, Corfu et al., 1989; Mortensen, 1992a,b). However, the plutonic activity lasted at least until 2.64 Ga (Machado et al., 1992), the age of post-tectonic two-mica granitoid plutons in the Lacorne tectonic block, northwest of Val-d'Or (Fig. 1).

Gold deposits in the Abitibi Subprovince are most abundant within or immediately north of the Cadillac-Larder Lake fault zone, which bounds the southern Abitibi and the metasedimentary Pontiac Subprovinces (Fig. 1). The mineralization is frequently concentrated in quartz veins crosscutting both supracrustal volcano-sedimentary assemblages and tonalitic intrusions. The mineralized tonalite-trondhjemite plutons are syn-volcanic (Corfu et al., 1989; Wong et al. 1991; Mortensen, 1992b) and generally thought to represent subvolcanic magma chambers related to overlying volcanic rocks. For example, the Flavrian-Powell plutons in the Rouyn-Noranda mining camp and the Bourlamaque pluton near Val-d'Or (Fig. 1) both yielded U-Pb ages of 2700 Ma (Claoué-Long et al., 1990; Wong et al. 1991; Mortensen, 1992b) that are identical to the age of adjacent volcanic rocks (Corfu et al., 1989; Wong et al. 1991).

The Silidor gold deposit is hosted by the Powell tonalitic intrusion (Fig. 1), a pluton which intrudes mafic to felsic lava flows of the Blake River Group. The deposit consists of a 900 m long gold-bearing quartz vein having a mean thickness of 3 m and dipping from 55° to 70° ENE (Picard, 1990). The host tonalite is altered over a distance of 30 m on both sides of the vein where the feldspars are strongly hematized. The ore zone has been divided into four facies (Picard, 1990) from the hematized tonalite inwards: 1) a ~2 m wide zone of tonalite with quartz-pyrite veinlets; 2) a ~0.5 m wide zone of carbonate-fuchsite breccia; 3) the gold-bearing quartz veins where samples were collected; and 4) a quartz cement breccia up to 8 m thick that formed in response to hydraulic fracturing. Native Au in the quartz veins is mainly associated to pyrite (both as inclusions or discrete grains) but minor amounts are also found in the gangue carbonates and silicates (Picard, 1990).

The Launay Au-Mo prospect is hosted in the Taschereau tonalite which intrudes mafic volcanic rocks north of Rouyn-Noranda (Fig. 1). The pluton is dated at 2718±2 Ma (Frarey and Krogh, 1986) and it consists of diorite, tonalite and trondhjemite cut by a granitic stock. The stock exposes an albite-rich aureole all along its contact with the Taschereau tonalite. A two-stage model was proposed by Jébrak and Harnois (1991) to explain the emplacement of the intrusive suite. Based on trace element abundances, these authors suggest that the Taschereau granitic rocks were derived from partial melting of the pre-existing tonalitic rocks, thus that the rock types do not represent end-members of a single magma that evolved through fractional crystallization.

The ore zone of the Launay prospect occurs in the albite-rich rocks at the contact of the granite with the tonalite (Jébrak, 1992). The mineralized zone has suffered pervasive sodic and potassic alteration. The core of that zone, which has been called an "episyenite", mainly consists of albite, quartz, white mica, calcite, magnetite and rutile (Jébrak, 1992). Gold is associated with pyrite and molybdenite. A potassic transition zone surrounds the episyenite which grades outwards into a chlorite-magnetite zone. Unlike most Au-bearing quartz veins found in the Abitibi Subprovince, this mineralization seems to lack any structural controls and has more affinities with porphyry type deposits (Jébrak, 1992). The rocks that have been collected from the Taschereau stock include fresh samples of the tonalite and the granite, and the episyenite.

## ANALYTICAL TECHNIQUES

Mineral separation was done using heavy liquids and a magnetic separator. Between 3 and 20 mg of unaltered grains of K-feldspar, plagioclase, quartz, chlorite, epidote, apatite, pyrite, hematite and molybdenite (100-200 μg), were hand-picked under a binocular microscope and washed with distilled water in an ultrasonic bath. Except for quartz and epidote, all silicates were powdered in an agate mortar and leached with a diluted HF-HBr solution for 30 minutes. The supernate was recovered and the residue was dissolved in hot concentrated HF. Hematite and apatite were completely dissolved after the initial washing treatment, while pyrite and molybdenite were leached with $HNO_3$ and HCl. Lead separation followed the technique of Manhès et al. (1980) and the isotopic compositions were determined using thermal ionisation mass spectrometry. The raw data were corrected for instrumental mass fractionation using factors of 0.09% and 0.24% $amu^{-1}$ for the Faraday and Daly detectors, respectively. Total Pb blanks were smaller than 70 pg and negligible. All regressions were calculated according to the method of York (1969) and the decay constants of Steiger and Jäger (1977). All errors are quoted at 95% level of confidence.

## RESULTS

*Silidor*

The Pb isotopic results from Silidor are listed in Table 1 and shown in Fig. 2. Pyrite has yielded $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios ranging from 25.2 to 44.5, 16.6 to 19.9 and 43.1 to 58.1, respectively. The four results for pyrite are well correlated in the $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram with a slope corresponding to an age of 2561±29 Ma (MSWD=0.8). Quartz yielded the least radiogenic composition, with Pb isotopic ratios only slightly higher than those of K-feldspar from granitoid rocks of the Abitibi (Gariépy and Allègre, 1985; Carignan et al., 1992), while chlorite yielded values intermediate between quartz and pyrite (Table 1). The data for pyrite, quartz and chlorite are collinear (Fig. 2a) and the slope of the isochron corresponds to an age of 2562±15 Ma (MSWD=0.5). Figure 2b shows the data in a $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram where they are also positively correlated. The slightly more scattered distribution of the data points can be attributed to small variations of the Th/U ratio of the different minerals. The line fitting the data points corresponds to a mean Th/U ratio of ~3.1.

*Taschereau tonalite*

Leachates and residues of K-feldspar (KF) separated from the tonalites have yielded $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios ranging from 13.56 to 18.16, 14.52 to 15.47 and 33.34 to 36.51, respectively (Table 1). Except for the least radiogenic residue (KF-164), the compositions of the KF are generally more radiogenic than those from any other intrusion of the Abitibi belt (Gariépy and Allègre, 1985; Carignan et al., 1992) and do not represent the initial Pb isotopic composition of the tonalite. The data are positively correlated in the $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram (Fig. 3) and the slope of the isochron corresponds to an age of 2.82±0.10 Ga (MSWD=0.5). The scatter of the data points can be attributed to analytical error alone, but the isochron remains much less precise than the U-Pb zircon age of the tonalite (2718±2 Ma; Frarey and Krogh, 1986) because the spread of the data points in Fig. 3 is not sufficiently large to better define the slope of the isochron.

*Taschereau granite*

K-feldspars separated from the granite samples also yielded Pb isotopic ratios slightly more radiogenic than KF from other granitoids of the belt (Table 1). Epidote from the granite has yielded Pb isotopic ratios comparable to that of KF-164 from the tonalite, suggesting derivation from a similar source, while apatite has the most radiogenic compositions. Epidote, K-feldspar and apatite are well correlated in the $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ (Fig. 4a) defining an age of 2710±26 Ma (MSWD=0.8), undistinguishable within errors from the U-Pb age of the Taschereau tonalite.

*Launay episyenite*

Three drill core samples of the mineralized episyenite were analyzed (Table 1) and the results are shown on Fig. 4b. The feldspars from the episyenite have the least radiogenic compositions and the sulfides and oxides the most. The data define a linear array in the $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram of Fig. 4b with a slope corresponding to an age of 2.60±0.05 Ga. However, the scatter of the data (MSWD=10) greatly exceeds that of analytical error alone, as all results obtained on molybdenite plot statistically above or below the regression line. Exclusion of the molybdenite data would yield an age of 2612±36 Ma (MSWD=2.7) which remains, within errors, significantly younger than that of the host tonalite and granite.

Figure 5 shows the Pb isotopic composition of the least radiogenic K-feldspars and epidote from the episyenite, the tonalite and the granite, and of the quartz from the Silidor deposit. These are compared to the compositional domain of mantle derived rocks, defined by the initial Pb isotopic composition of mafic and ultramafic rocks in the Abitibi (Brévart et al., 1986; Deloule et al., 1989; Dupré and Arndt, 1990), and to the crustal domain delineated by the initial composition of sediments, high-grade gneisses and two-mica granites (Gariépy and Allègre, 1985; Deloule et al., 1989; Carignan et al., 1992). The tonalite and the granite KF plots only slightly above the mantle domain (Fig. 5); this composition is typical of almost all tonalite-trondhjemite bodies of the Abitibi greenstone belt (Carignan et al., 1992). This is interpreted to reflect a magmatic derivation from dominantly juvenile igneous sources. The K-feldspars from the episyenite are much more radiogenic than those of the tonalite and the granite. The leachates of this mineral were always very radiogenic and some radiogenic Pb may still have been present in the residue and the analytical results probably only record the maximum value of the initial ratio. Nevertheless, projection of the alignment towards unradiogenic values clearly show that the episyenite has a high initial $^{207}Pb/^{204}Pb$, typical of crustally derived rocks.

The results obtained on K-feldspar and plagioclase are positively correlated in a $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (not illustrated) and correspond to a Th/U ratio of ~2.9. However, the data for molybdenite are not correlated, thus confirming that this mineral may be perturbed.

# DISCUSSION

*The Pb-Pb ages*

In terms of absolute age determination, the significance of Pb-Pb ages obtained on ore minerals is disputable because sulfides and oxides may have low closing temperatures of U and Pb diffusion. For example, in areas where the rate of uplift is very slow, the Pb-Pb isochrons obtained on these minerals may simply record cooling below a given isotherm, yielding thus apparent ages younger than that of the mineralizing event. Similarly, any younger thermal event bringing the minerals above their closing temperature of diffusion may partially or totally reset the isotopic system as speculated by Kerrich (1986), Kerrich et al. (1987) and Claoué-Long et al. (1990) for some U-Pb, Ar-Ar and Sm-Nd ages in the range of 2630 to 2550 Ma obtained on minerals associated to Abitibi gold deposits.

In the presence of a secondary reset Pb-Pb system one would expect to observe, under ideal circumstances, discrete alignments on the $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagrams, defined by different minerals, which would correspond to the time when a given mineral species was sufficiently cold to become closed to U and/or Pb diffusion. Those minerals with lower closing temperatures should thus record younger ages if slow cooling rates prevailed or if they were reset by repeated pulses of hydrothermal activity. More likely, a scattering of the data would be expected reflecting various disequilibrium processes such as open system behavior, variable diffusion rates as a function of grain size and potential uptake of labile radiogenic Pb.

The Au-bearing pyrite and the chlorite at Silidor define a single, well correlated line with quartz indicating that these minerals all have the same age and initial isotopic composition. This either implies that the formation of the Au-bearing quartz vein occurred *ca.* 140 Ma after the intrusion of the Powell tonalite or that it was completely isotopically reset close to 2.56 Ga.

The Launay Au-Mo deposit has had a more complex history as indicated by the pervasive sodic and potassic alteration events which may, for example, represent distinct hydrothermal pulses separated by long periods of time. This scenario has been suggested by

Claoué-Long et al. (1990) for gold deposits around Val-d'Or, based on a variety of U-Pb ages of zircons found within quartz-tourmaline mineralized veins. However, Davis and Corfu (1991) argue that this variety is likely an artifact of imprecision, discordance and zircon inheritance in mineralized veins. Franklin et al. (1983), using Pb isotopes, also reported a number of gold deposits in southern Abitibi that have suffered post-crystallization remobilization and their data fit an age of *ca.* 2.2 Ga for the remobilization.

At Launay, the ore-bearing episyenite systematically occurs at the contact between the granite and the tonalite. This supports the idea that the hydrothermal systems was driven by heat released during granite cooling rather than by a younger event of unknown origin. Thus, the age of 2.61 Ga obtained on the Launay ore minerals probably does not record the initial alteration event related to granite emplacement.

The K-feldspar in the Launay ore zone is more radiogenic than that of the host tonalite and the granite (Fig. 5). Two hypotheses can be put forward to explain this situation. One may assume that the ore was initially deposited at 2.7 Ga with an initial composition comparable to that of the granite or the tonalite and completely re-homogeneized during a thermal perturbation at *ca.* 2.6 Ga. The difference in the initial isotopic compositions of the ore and the granite would then be due to radioactive growth in the ore zone during the 2.7 Ga to 2.6 Ga time interval. If such was the case, the ore zone must have had a $^{238}U/^{204}Pb$ ratio greater than 35 before the Pb was redistributed amongst the different minerals. This is unlikely because most of the mineral analyzed thereafter had $^{238}U/^{204}Pb$ ratios well below 35. More likely, the high $^{207}Pb/^{204}Pb$ ratios in the K-feldspar of the Launay ore zone and in the quartz of the Silidor deposits indicate that the fluids came from source reservoirs having an isotopic composition similar to the crustal domain of Fig. 5. This implies that the Pb in the mineralizing fluids was not derived from the immediate host rocks. This situation has been recognized in other isotopic studies of minerals from Au deposits. For example, Kerrich and Fryer (1979) and Kerrich (1983, 1986) have shown that Au-bearing quartz veins in the Abitibi belt have a narrow range of $\delta^{18}O$ values (from 12.5 to 15 ‰) that are always different from that of unmineralized host rocks.

If this interpretation is correct, then some constraints can be placed on the age of the two deposits. This is because Carignan et al. (1992) have reported a marked change in the Pb isotopic composition of the Abitibi reservoirs as a function of time. Prior to 2.68 Ga, all granitoid rocks in the Abitibi were derived from a source reservoir having Pb isotopic compositions comparable to the mantle reservoir or plotting only slightly above it. The only granitoid rocks having initial Pb isotopic compositions similar to the crustal domain are late-tectonic bodies intruded between 2.68 and 2.64 Ga in the Abitibi and Pontiac Subprovinces. This change in source composition as a function of time most likely reflects the tectonic juxtaposition of Abitibi volcano-sedimentary assemblages over older basement rocks. The two deposits studied here must have formed after 2.68 Ga in order that the hydrothermal fluids acquire the isotopic signature of this older reservoir.

Whether the Pb-Pb isochron determined here records the primary age of ore deposition or secondary thermal reset remains unsettled. Evidence for late regional metamorphism outside the Cadillac-Larder Lake fault zone and the Lacorne block is scanty but not absent. Brévart et al. (1986) have reported sulfide-whole rock Pb-Pb isochrons of 2580±20 Ma and 2430±130 Ma for Fred's Flow and Theo's Flow komatiites in southern Abitibi that were interpreted as the age of alteration related to regional metamorphism. The results presented here support the concept of widespread very low-grade regional metamorphism affecting the entire Abitibi belt for some 60 to 100 Ma after its formation. This event may be related to tectonic jostling at the periphery of the belt as granulite terranes surrounding the Abitibi, like the Kapuskasing uplift to the west and the Grenville Front Tectonic Zone to the southeast, have yielded U-Pb and Pb-Pb ages in the range of 2640 to 2580 Ma (Corfu 1987; Gariépy et al. 1990; Philippe et al., 1992) indicating that metamorphic activitiy in the lower crust continued long after magmatic activity ended at higher crustal levels.

*The sources of gold*

Figure 6 is a $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ compilation diagram showing the Pb isotopic composition of gold deposits in the Superior Province hosted in a variety of supracrustal lithologies. The initial Pb isotopic compositions of the dated deposits (U-Pb and Pb-Pb) has been calculated using the intersection of the geochron with an isochron drawn through available Pb-isotopic data. For undated deposits, the least radiogenic results have been used. The diagram shows that Au deposits hosted in volcano-sedimentary assemblages have a wide compositional range, extending from values typical of juvenile mafic rocks towards that of ancient crustal rocks. The compositional domain of gold deposits hosted in granitoids is somewhat more restricted, plotting at positions intermediate between the mantle and crustal domains as well as within the crustal domain.

Quite clearly, the Pb isotopic data obtained on gold deposits are consistant with all metallogenic models outlined in the introduction. For example, the less radiogenic, volcanic hosted gold deposits may be of an entirely magmatic origin. Alternatively, they could have formed by the circulation of fluids generated by prograde metamorphism at the base of the greenstone assemblage, as suggested by Groves and Phillips (1987), assuming progressively the mean Pb isotopic composition of the supracrustal lithologies. However, the more radiogenic deposits are best explained by a model relating the formation of mineralizing fluids to deep crustal processes after 2.68 Ga. Evolved crustal material underlying the Abitibi greenstone belt has only been indirectly identified, but Jackson and Sutcliffe (1990) proposed evidence for the overthrust of the southern Abitibi onto the Pontiac after 2.7 Ga.

## CONCLUSIONS

The high degree of correlation of pyrite, chlorite and quartz from the Silidor deposit in the Pb-diagrams supports the idea that the age of these minerals is not the result of secondary alteration. The 2562±12 Ma isochron thus either represents the age of Au deposition, or a complet reset of the U-Pb system *ca.* 140 Ma after the intrusion of the host tonalite. Minerals from the Launay deposit are not so well correlated in the Pb-isochron diagram and the age of 2612±36 Ma does not record the initial alteration event related to granite emplacement. The least radiogenic Pb-isotopic ratios measured in the two studied deposits indicate that the mineralizing fluids came from source reservoirs having an isotopic composition similar to the crustal domain of the Abitibi belt. This implies that the Pb in the fluids was not derived from the immediate host rocks. As the only granitoid rocks having initial Pb isotopic composition similar to the crustal domain are late-tectonic bodies intruded between 2.68 and 2.64 Ga, the two deposits studied here must have formed after 2.68 Ga in order that the hydrothermal fluids acquire the isotopic signature of this radiogenic reservoir.

Ages younger than 2.6 Ga were up now mainly found in the vicinity of the Cadillac-Larder Lake break. The results obtained at Launay supports the concept of widespread regional metamorphism affecting the entire Abitibi belt for some 60 to 100 Ma after its formation.

The initial Pb isotopic composition of many gold deposits from the Superior Province has been used to characterize the source regions of Au deposits. Gold bearing quartz veins hosted in volcano-sedimentary assemblages have a wide compositional range, extending from values typical of juvenile mafic rocks towards that of ancient crustal rocks. The compositional domain of gold deposits hosted in granitoids is somewhat more restricted, plotting at positions intermediate between the mantle and crustal domains as well as within the crustal domain. These data support the concept that there is no single model of gold emplacement applicable to all deposits. The less radiogenic, volcanic hosted Au deposits may be of an entirely magmatic origin or formed by the circulation of fluids generated by prograde metamorphism at the base of the greenstone assemblage assuming progressively the mean Pb isotopic composition of the supracrustal lithologies. However, the more radiogenic deposits are best explained by a model relating the formation of mineralizing fluids to deep crustal processes after 2.68 Ga.

## ACKNOWLEDGMENTS

The authors are grateful to the financial support of the Natural Sciences and Engineering Research Council (NSERC) of Canada and the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (FCAR) of Québec. We are also thankful to the staff of Silidor Mine and to M. Jébrak for providing samples, and to R.K. Stevenson for his comments on the manuscript. Laboratory expenses at GEOTOP are covered by infrastructure grants from NSERC and FCAR.

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## FIGURE CAPTIONS

Fig 1. Geological map of the south-central Abitibi Subprovince showing the location of granitoid hosted gold and molybdenum deposits and the Silidor and Launay gold deposits; modified from Rive et al. (1990) and Jébrak (1992).

Fig. 2. a) $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram showing that the data obtained on quartz, chlorite and Au-bearing pyrite fit a single line corresponding to an age of 2562±12 Ma. b) $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram showing that the linear distribution of the data points corresponds to a Th/U ratio of 3.1.

Fig. 3. $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagrams showing the results for K-feldspar from the Taschereau tonalite; filled symbols = residues, open symbols = leachates.

Fig. 4. $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagrams showing the results for a) epidote, K-feldspar and apatite from the granite and b) K-feldspar, plagioclase, molybdenite, pyrite and hematite from the episyenite.

Fig. 5. $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram showing the composition of the least radiogenic K-feldspars and epidote from the ore zone, the tonalite and the granite of the Launay prospect, and of the quartz of the Silidor deposit. These are compared to the compositional domains of the Abitibi mantle and crust in the late Archean. A 2.7 Ga reference isochron is shown for reference.

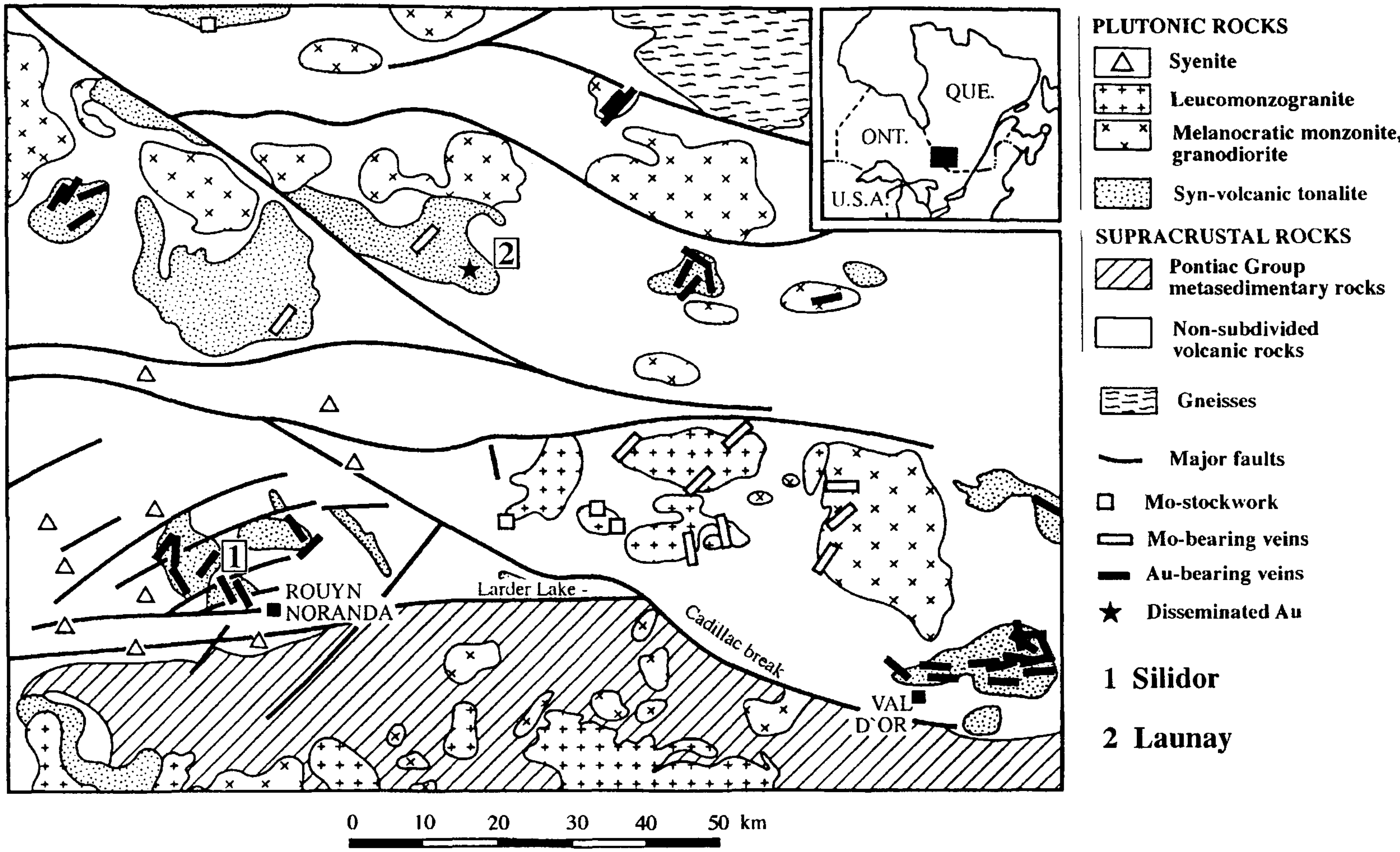
Fig. 6. $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram showing the Pb isotopic composition of gold deposits in the Superior Province hosted in a variety of supracrustal lithologies. The mantle and crustal compositional domains of the Abitibi belt are shown are shown for comparison. Circles: Au deposits hosted in volcano-sedimentary assemblages (data from Deloule et al. 1989; Corfu and Muir 1989; Wong et al. 1991; Franklin et al. 1983); squares: Au deposits

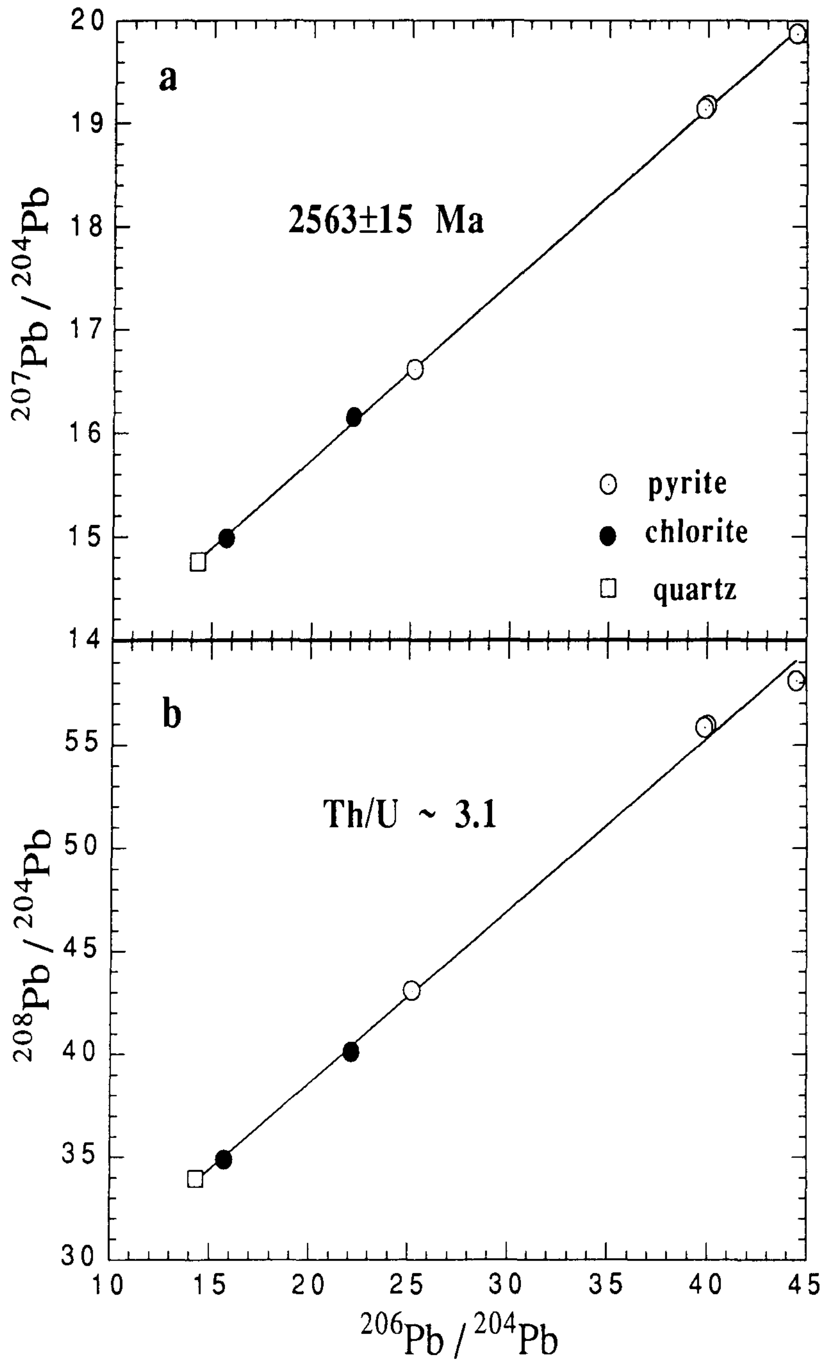
hosted in granitoids (Jemielita et al. 1990; Franklin et al. 1983); triangles: Silidor and Launay gold deposits (this study).

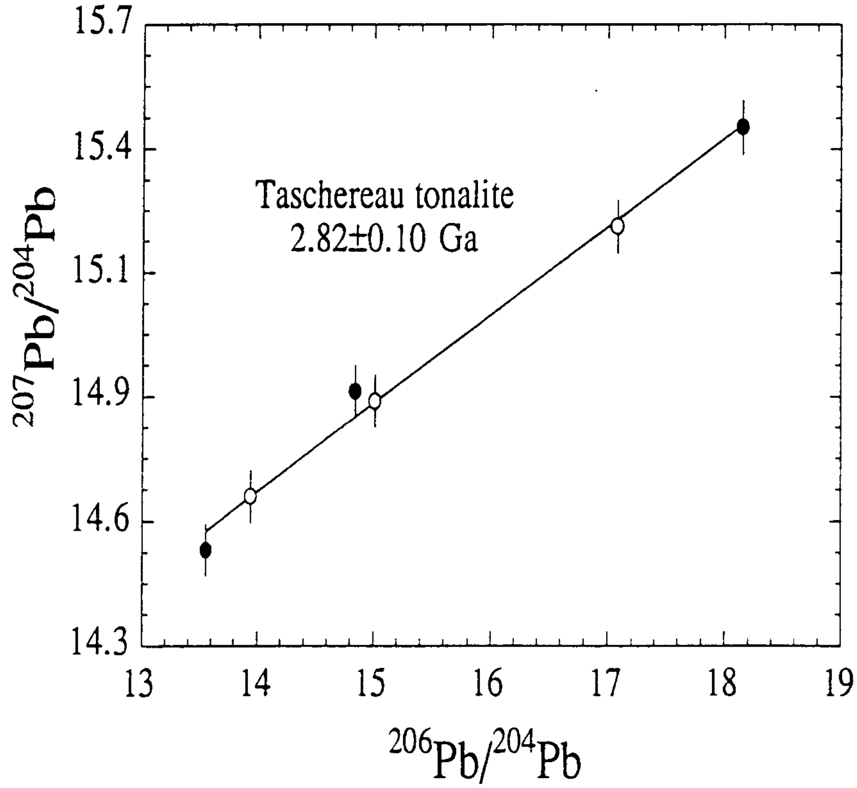
Table 1. Pb isotopic results

| Locality | mineral | 206Pb/204Pb | 207Pb/204Pb | 208Pb/204Pb |
|---|---|---|---|---|
| Silidor | py-1/B | 39.856 | 19.140 | 55.820 |
| | py-1/R | 40.016 | 19.174 | 55.904 |
| | py-1/L | 44.514 | 19.869 | 58.081 |
| | py-2/B | 25.213 | 16.610 | 43.059 |
| | quartz/B | 14.310 | 14.761 | 33.944 |
| | chl/R | 15.761 | 14.982 | 34.863 |
| | chl/L | 22.150 | 16.149 | 40.087 |
| Taschereau | | | | |
| *tonalite* | KF-164/R | 13.557 | 14.516 | 33.337 |
| | KF-164/L | 13.945 | 14.635 | 33.679 |
| | KF-144/R | 14.841 | 14.871 | 33.972 |
| | KF-144/L | 15.012 | 14.849 | 34.075 |
| | KF-110/R | 18.155 | 15.468 | 36.506 |
| | KF-110/L | 17.083 | 15.245 | 35.630 |
| *granite* | KF-143/R | 14.106 | 14.619 | 33.622 |
| | KF-143/L | 14.101 | 14.689 | 33.932 |
| | KF-140/L | 14.123 | 14.666 | 33.767 |
| | epi-91/B | 13.718 | 14.524 | 33.249 |
| | ap-91/B | 34.397 | 18.414 | 41.159 |
| *episyenite* | he-293/B | 30.062 | 17.647 | 41.883 |
| | KF-293/R | 14.422 | 14.835 | 34.196 |
| | pl-293/R | 14.683 | 14.841 | 34.489 |
| | pl-293/L | 17.904 | 15.539 | 36.983 |
| | KF-290/R | 14.873 | 14.868 | 34.698 |
| | KF-290/L | 17.259 | 15.575 | 37.093 |
| | mo-290/B | 28.530 | 17.208 | 41.665 |
| | mo-290/R | 40.031 | 19.665 | 39.332 |
| | mo-290/L | 29.721 | 17.219 | 45.415 |
| | KF-22/R | 15.486 | 15.102 | 34.958 |
| | KF-22/L | 16.762 | 15.378 | 36.161 |
| | pl-22/R | 17.038 | 15.334 | 36.616 |
| | pl-22/L | 18.245 | 15.672 | 36.959 |
| | py-22/B | 38.433 | 19.043 | 63.291 |
| | mo-22/B | 21.186 | 15.876 | 36.954 |

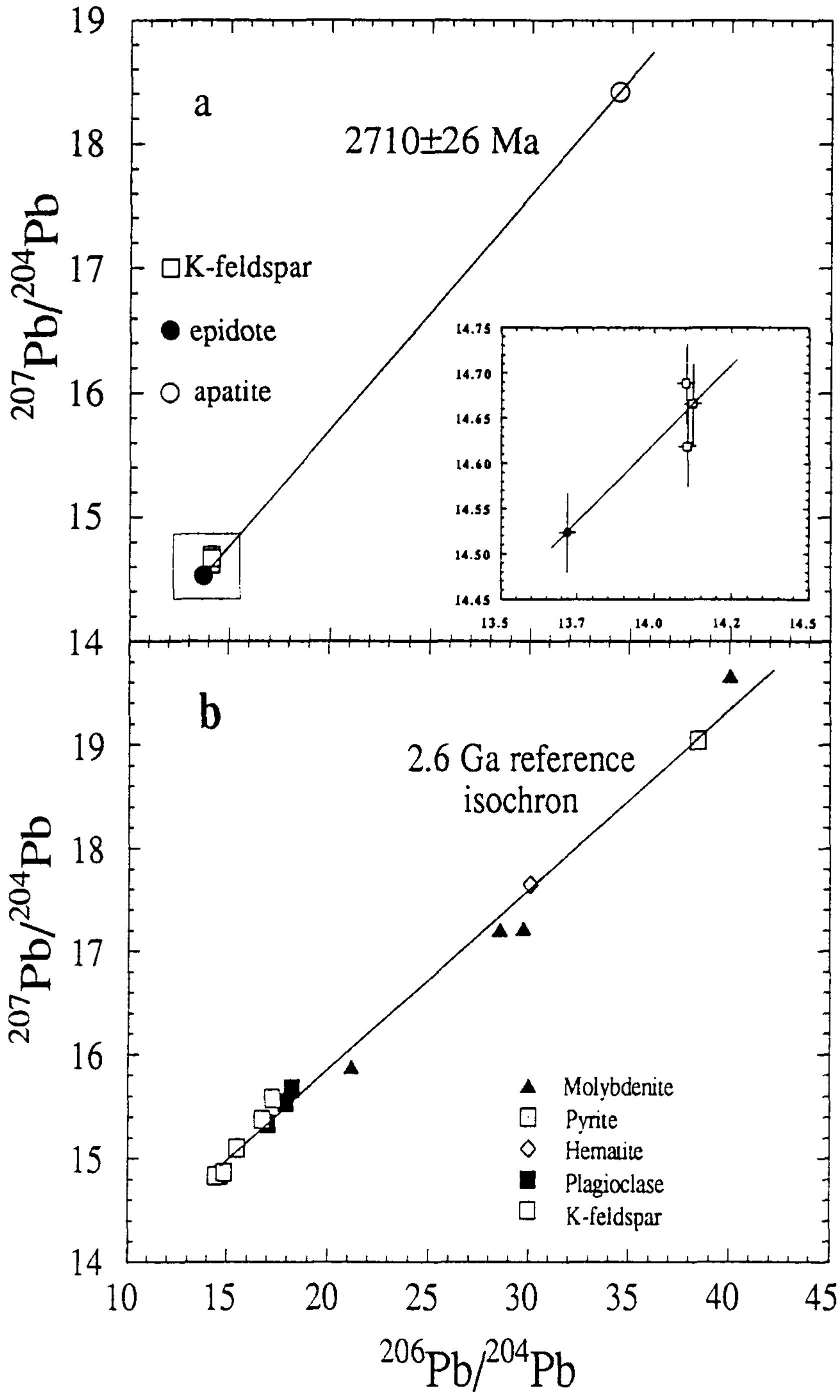
B: bulk; R: residue; L: leachate; py: pyrite; chl: chlorite; KF: K-feldspar
he: hematite; pl: plagioclase; epi: epidote; ap: apatite; mo: molybdenite.
The number following the mineral from Taschereau is the sample number.
Silidor: pyrite-1: 0.5 amp magnetic fraction; pyrite-2: non magnetic fraction.

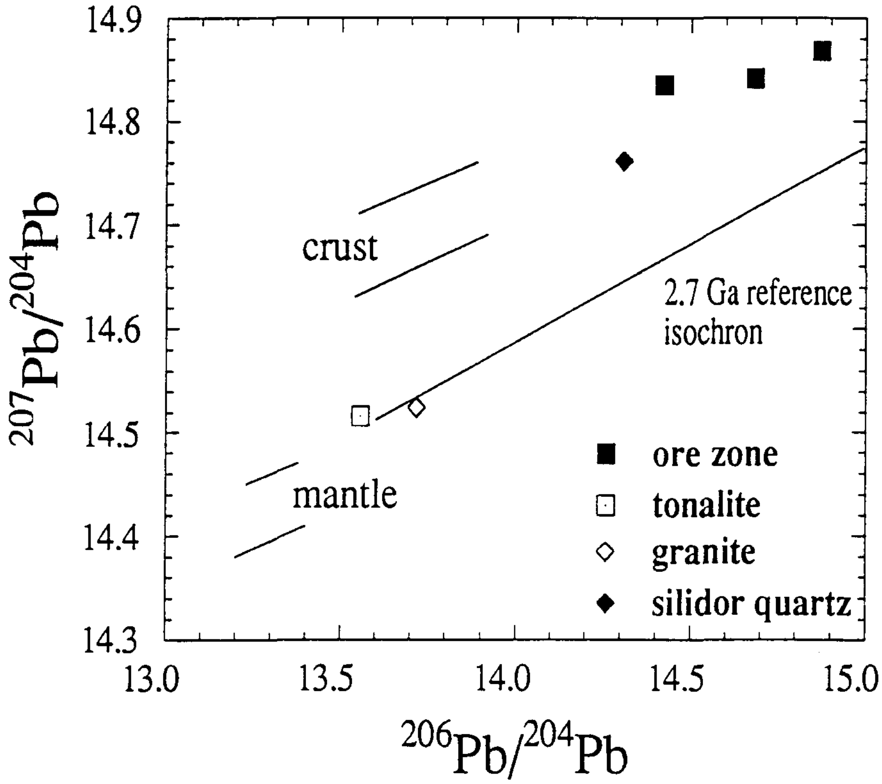

QUE.
ONT.
U.S.A.
ROUYN
NORANDA
Larder Lake
Cadillac break
VAL D'OR
PLUTONIC ROCKS
Syenite
Leucomonzogranite
Melanocratic monzonite, granodiorite
Syn-volcanic tonalite
SUPRACRUSTAL ROCKS
Pontiac Group metasedimentary rocks
Non-subdivided volcanic rocks
Gneisses
Major faults
Mo-stockwork
Mo-bearing veins
Au-bearing veins
Disseminated Au
1 Silidor
2 Launay
0 10 20 30 40 50 km

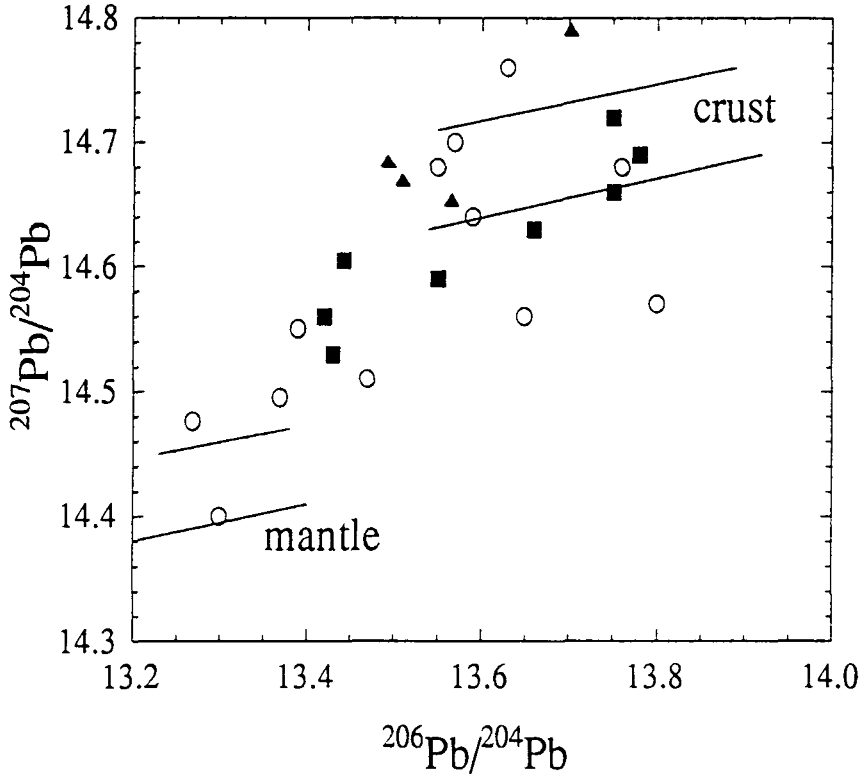

a
2563±15 Ma
pyrite
chlorite
quartz
$^{207}Pb / ^{204}Pb$
b
Th/U ~ 3.1
$^{208}Pb / ^{204}Pb$
$^{206}Pb / ^{204}Pb$



Taschereau tonalite
2.82±0.10 Ga
15.7
15.4
15.1
14.9
14.6
14.3
13
14
15
16
17
18
19
207Pb/204Pb
206Pb/204Pb


a
2710±26 Ma
K-feldspar
epidote
apatite
$^{207}Pb/^{204}Pb$
b
2.6 Ga reference isochron
Molybdenite
Pyrite
Hematite
Plagioclase
K-feldspar
$^{207}Pb/^{204}Pb$
$^{206}Pb/^{204}Pb$


14.9
14.8
14.7
14.6
14.5
14.4
14.3
13.0
13.5
14.0
14.5
15.0
$^{207}Pb/^{204}Pb$
$^{206}Pb/^{204}Pb$
crust
mantle
2.7 Ga reference isochron
ore zone
tonalite
granite
silidor quartz



14.8
14.7
14.6
14.5
14.4
14.3
13.2
13.4
13.6
13.8
14.0
crust
mantle
$^{207}Pb/^{204}Pb$
$^{206}Pb/^{204}Pb$

# Pb isotopic composition of Ni-Cu and Pb ore deposits in an Archean greenstone belt: Evidence for Proterozoic remobilization in the Pontiac Subprovince of Canada

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Accepted for publication by: *Economic Geology*

## Introduction

In order to understand the genesis of ore deposits, it is fundamental to know the age of formation and the source of mineralization. Chemical tracers like Pb isotopes are a privileged tool for this type of study because 1) traces of Pb are frequently present in ore bearing minerals; 2) the initial isotopic composition of minerals yields access to the time integrated $^{238}U/^{204}Pb$ ($\mu_1$) of the source regions; 3) the short half life of $^{235}U$ allows the formation of reservoirs with highly contrasted Pb isotopic compositions in the Archean; and 4) traces of U in some minerals allows the *in situ* growth of radiogenic Pb that can be used to define Pb-Pb isochrons.

Isotopic studies on mineralized rocks of the Abitibi greenstone belt of Canada have demonstrated that mineralization associated with mafic and felsic volcanic rocks has a juvenile character, with Pb initial compositions similar to those of U-poor sulfides from komatiitic lava flows (Brévart et al., 1986; Deloule et al., 1989; Dupré and Arndt, 1991). On the other hand, minerals from banded iron formations and mineralization associated with late granitoid intrusions and pegmatites have a more radiogenic Pb composition, suggesting a derivation from older crustal segments within the belt (Deloule et al., 1989; Carignan et al., 1992).

A detailed study of Pb isotopes in granitoids from the Abitibi and the Pontiac Subprovinces (Carignan et al., 1992) has shown that most of the syn- to late-volcanic plutons, intruded between 2720 and 2685 Ma (Machado et al., 1992; Mortensen, 1992a,b), have a source reservoir with an important juvenile component, while post-volcanic K-rich plutons and pegmatites intruded between 2680 Ma and 2640 Ma (Machado et al., 1991, 1992) have more radiogenic initial compositions interpreted as involving the recycling of older crustal segments. This recycling is volumetrically important in the Pontiac because more than half of the Subprovince consists of these late granitoids (Rive et al., 1990).

The Baby-Belleterre (BB) belt is a greenstone terrane within the Pontiac very similar to the Abitibi belt in both lithology and mineralization. This volcanic belt may represent a klippe of supracrustal material related to igneous rocks of similar age in the Abitibi

Subprovince (Rive et al., 1990). Different volcanic-related ore deposits have been sampled throughout the BB belt, and were analyzed for their Pb isotopic composition in order to 1) determine the age of ore formation; 2) characterize the source regions of the metals; 3) compare the Pb composition of the BB mineralizations to those of the Abitibi; and 4) place the mineralizing events in a tectonic framework.

## Geological Setting

The Baby-Belleterre volcano-sedimentary belt is located in the southern part of the Pontiac Subprovince (Fig. 1). It consists of three distinct portions known as the Baby, Lac des Bois and Belleterre groups (Hocq, 1990). The east-west belt is bounded to the south-southeast by the Grenville Front tectonic zone, to the west by Huronian sedimentary rocks, and to the north by granitoids of the Pontiac Subprovince (Fig. 1). Sediments of the Pontiac Group are also found all around the belt.

The BB belt consists mainly of pillowed island-arc tholeiites with minor dacites and rhyolites, conglomerates and volcanoclastic sediments (Hocq, 1990; Barnes et al., 1991), intruded by tonalitic and dioritic-granodioritic plutons and smaller bodies of anorthositic gabbro (Rive et al., 1990). Komatiites are found along the northern edge of the Baby group, which are in direct contact with the Pontiac sedimentary rocks. The komatiites are depleted in Al and LREE, and show no evidence of contamination from the sediments (Barnes et al., 1991). Dimroth et al. (1983) thought that the volcanic rocks of the Baby group were uncomformably deposited on the Pontiac sediments while Hocq (1990) and Rive et al. (1990) suggested that the volcanic rocks were thrusted onto the Pontiac Group.

U-Pb ages indicate that volcanism in the BB belt occurred between 2705 Ma and 2685 Ma (Machado et al., 1992). Two small plutons at the southern edge of the belt, intruded in the Pontiac sediments, have yielded younger U-Pb ages of 2678 Ma and 2669 Ma (Machado et al., 1992).

Four deposits have been sampled in the BB belt: the Kerr Adisson Ni-Cu prospect, the Cu Patry prospect, the Lorraine Cu-Ni Mine, and the Wright Pb Mine. The Kerr Adisson prospect, located in the northeastern part of the belt (Fig. 1), consists of lenses of disseminated sulfides (chalcopyrite, pyrrhotite, pyrite) within mafic volcanic rocks. The Patry prospect, located in the central part of the BB belt (Fig. 1), consists of a stockwork of disseminated chalcopyrite and pyrite within the Belleterre-Fugerville tonalite, the largest intrusive body in the belt, dated by the U-Pb method at 2705±3 Ma (Machado et al., 1992). The Lorraine Cu-Ni Mine, in the central part of the belt, is a massive sulfide lense of pyrrhotite and chalcopyrite with traces of magnetite deposited at the basal contact between a syn-volcanic gabbro sill and tholeiitic volcanic rocks. The deposit probably formed by sulfide segregation from the mafic magma (S.J. Barnes, personal communication, 1992) and it was subsequently deformed and hydrothermally altered. In the Lorraine Mine, calcite-galena-marcasite-silver veins crosscut the massive sulfides, the meta-andesites and the meta-diorites, and are possibly related to Huronian rocks outcropping in the area (Descarreaux, 1967). The Wright Pb Mine, located at the western border of the belt, along Lake Temiskaming, consists of galena-bearing carbonate breccias in mafic to intermediate volcanic rocks, which are overlain by Huronian sedimentary rocks of the Cobalt Group.

## Analytical Techniques

All samples were crushed and sieved to a grain size of 100 to 200 µm. Mineral separation was done with heavy liquids and a magnetic separator. Samples were handpicked under a binocular microscope and only unaltered grains were selected. Between 5 mg and 30 mg of pyrite, chalcopyrite, pyrrhotite, magnetite, carbonate, amphibole, and plagioclase were cleaned with distilled water in an ultrasonic bath. Some of these minerals were leached with hot $CH_3COOH$, HCl, HBr and HF acids and the supernates were recovered for Pb-isotope analyses before complete dissolution of the residues. The purpose of the leaching treatments was to maximize the spread of the Pb ratios in the isochron diagram in order to obtain better age precision. This is based on the concept that the radiogenic Pb component that developed in a mineral through U decay might be located in crystal regions that have suffered radiation damages (Deloule et al. 1989). The radiogenic Pb in these regions might thus be dissolved preferentially to the initial common Pb incorporated in the crystal lattice. Galena analyses were done using a single grain, approximately 0.1 mm in diameter, that was cleaned in 2N HCl, dissolved in 8N HBr and dried. The salt was then dissolved in 6N HCl and sonified for 5 minutes to homogenize the solution. An aliquot of this solution was directly used for isotopic analysis.

The separation of Pb followed the technique of Manhès et al. (1980) and the isotopic analyses were done on a VG SECTOR thermal ionisation mass spectrometer. Total Pb blanks were less than 5 pg for galena and 50 pg for the other minerals. The 2$\sigma$ uncertainties are 0.2, 0.3 and 0.4% for the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios, respectively. The fractionation correction applied is 0.09% amu$^{-1}$. These values have been determined by repeated measurements of the NBS SRM 981 standard using sample loads in the range of 10 to 150 ng, analyzed at temperatures of 1350 to 1500°C. Regression treatments were done with the method of York (1969) and the decay constants recommended by Steiger and Jäger (1977) were used for age calculations. The $\mu_1$ values were calculated using the isotopic composition of Canyon Diablo troilite (Tatsumoto et al. 1973) and 4.55 Ga as the age of the Earth. All errors are quoted at the 95% confidence level.

## Results

*Kerr Adisson Ni-Cu prospect*

Pyrite and pyrrhotite yield $^{206}Pb/^{204}Pb$ ratios between 14.78 and 17.71, $^{207}Pb/^{204}Pb$ between 14.77 and 15.35, and $^{208}Pb/^{204}Pb$ between 35.00 and 37.15 (Table 1). Amphibole from the same sample yields comparable compositions but plagioclase has much more radiogenic compositions. The data are positively correlated in a $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram (Fig. 2a) with a slope of 0.1843±0.0016 (MSWD = 9.4) which corresponds to an age of 2692±36 Ma. When the results obtained on K-feldspars from the nearby Belleterre-Fugerville tonalite (Carignan et al. 1992) are included in the regression, the slope of the line (0.1846±0.0014) and the MSWD value (5.9) remain comparable. This slope corresponds to an age of 2694±30 Ma which is identical within error to the U-Pb zircon age of 2705±3 Ma determined for the tonalite (Machado et al., 1992). This suggests that the tonalite and the ore minerals were derived from the same Pb reservoir whose time-integrated $^{238}U/^{204}Pb$ ratio ($\mu_1$) is 7.8. This value is within the range of those determined for Abitibi komatiites, between 7.6 and 7.8 (Dupré and Arndt, 1991). Therefore, the source of the mineralization has an important juvenile mantle component.

The data are not correlated in the $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram (Fig. 2b), but reference lines of different Th/U ratios passing through the initial composition of the tonalite have been drawn in the figure. The sulfides have a higher Th/U ratio (~3.8) than the silicates (~0.75), indicating a large fractionation of Th and U between the minerals.

*Patry Cu prospect*

Plagioclase, pyrite, and chalcopyrite from the deposit were analyzed and the results are shown on Fig. 3. Leachates and residues from three fractions of plagioclase have $^{206}Pb/^{204}Pb$ varying from 18.40 to 26.22, $^{207}Pb/^{204}Pb$ from 15.40 to 16.81, and $^{208}Pb/^{204}Pb$ from 36.01 to 41.91 (Table 1). The results for plagioclase and for K-feldspars from the host tonalite (Carignan et al., 1992) are positively correlated in a $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram along a line having a slope of 0.1894±0.0018 (MSWD = 6.5). This slope corresponds to an age of 2736±38 Ma that is identical within error to the U-Pb age of the host rock (Machado et al. 1992). The calculated $\mu_1$ of 7.8 is also indicative of a juvenile source for the tonalite. Pyrite and a mixed populations of pyrite and chalcopyrite were separated in different aliquots that were processed separately. Table 1 shows that the isotopic compositions determined for the bulk minerals are always intermediate between those obtained for the leachates, which yield the most radiogenic compositions, and the residues that are the least radiogenic. This suggests that the leaching treatments indeed removed radiogenic Pb components that are not tightly bound in the mineral structure.

Pyrite and chalcopyrite have very radiogenic Pb isotopic compositions (Table 1) that are positively correlated in a $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram (Fig. 3). The slope of the line is 0.1265±0.0008 (MSWD = 19) and corresponds to an age of 2050±48 Ma that is significantly younger than the host tonalite. The leachates from the mixed pyrite-chalcopyrite fractions yield the most radiogenic compositions and when they are omitted from the calculation of the regression, the line is better defined, the MSWD value dropping from 19 to 1.3. The slope (0.1356±0.0012) corresponds to an age of 2172±17 Ma, still very young compared to the host rock. Using this age, the sulfide minerals would have a low $\mu_1$ value of 7.3, which is much lower than the one inferred for the depleted mantle.

The data are not correlated in $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ space, suggesting large variation of the Th/U ratios between the different minerals.

*Lorraine Cu-Ni deposit*

Leachates and residues from pyrrhotite and magnetite yield similar isotopic compositions with $^{206}Pb/^{204}Pb$ varying from 18.04 to 19.47, $^{207}Pb/^{204}Pb$ from 15.53 to 15.72, and $^{208}Pb/^{204}Pb$ from 37.70 to 38.47 (Table 1). In contrast to the pyrite-chalcopyrite samples from the Patry prospect, the residues of magnetite and pyrrhotite from the Lorraine deposit are consistently more radiogenic than the leachates. The results are correlated in the $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram (Fig. 4) with a slope corresponding to an age of 2.0±0.2 Ga Ma and a $\mu_1$ of ~8.2. The large error is due to the small spread of the data. Nevertheless, this age is also younger than those for the BB belt.

The data are not correlated in a $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram, suggesting variations of the Th/U ratio between and within the minerals.

*Wright Pb Mine*

Three samples of galena have comparable Pb isotopic compositions with mean $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios of 14.68, 15.07, and 34.21 respectively. These values are compatible with a Proterozoic but not an Archean age. Carbonates have similar compositions but slightly higher $^{207}Pb/^{204}Pb$ values, suggesting a more radiogenic Pb source than for the galena (Table 1). These data are presented in Fig. 5a along with the composition of galena from Proterozoic Cobalt vein deposits (Franklin et al., 1983) found within sedimentary rocks of the Cobalt Group, west of the Wright Mine. A 2.2 Ga reference isochron and the 2.1 and 2.0 Ga geochrons are also shown in Fig. 5a. All the data plot close to the geochrons suggesting various Pb sources for the deposits. The Pb mineralization hosted in the volcanic rocks of the Wright Mine is the least radiogenic whereas Pb from mineralized veins hosted in metasediments shows the most radiogenic compositions. This indicates that the Pb was derived from a local source, probably the host rocks of the deposits.

The galena Pb ratios would fit a $\mu_1$ of ~8 in the diagram of Fig. 5a, and plot on the extension of the regression line passing through the data points of the Lorraine Mine. When samples from both mines are regressed together, the slope of the line (0.134±0.005; MSWD = 0.6) corresponds to an age of 2210±40 Ma, with a $\mu_1$ of 8.2 (Fig. 5b). This age is similar to that obtained with data from the Lorraine mine alone. However, as the Huronian mineralizing event may have remobilized Pb at a local scale, fluids that circulated in each deposit may have had different isotopic compositions. The 2210 Ma age is also within error to the 2172 Ma age for the Patry sulfides and the large difference between the $\mu_1$ values for these deposits supports again a local origin for the Pb composition of the mineralizating fluids.

## Discussion

The observation that three ore deposits out of four, covering a wide area of the BB greenstone belt, have Proterozoic Pb isotopic compositions is remarkable. The only deposit that preserved an Archean signature is the Kerr Adisson Ni-Cu prospect. At this locality, Pb isotopes show that the silicates and sulfides are cogenetic and that the ore is "purely" magmatic. The deposit has not been affected by surrounding post-volcanic K-rich plutons, intruded between 2680 Ma and 2650 Ma (Machado et al,. 1992), and which have yielded a more radiogenic initial Pb composition (Carignan et al., 1992). The time-integrated $\mu_1$ of the source reservoir, identical to that determine for the Abitibi mantle (Dupré and Arndt, 1991), suggests a derivation from a juvenile component or a mantle-derived rock with a short time of residence in the crust. This supports the idea that the mineralizing magmas and fluids did not circulate through an older evolved crust, and that the BB greenstone belt may be allochtonous. This also agrees with the tectonic model of Jackson and Sutcliffe (1990), proposing that the Abitibi overthrusted the Pontiac in late Archean time. Therefore, the BB greenstone belt may represent a remnant of the Abitibi in the Pontiac Subprovince (Rive et al., 1990).

Pb isotopic data indicate that thermal events during the Proterozoic have driven the formation of hydrothermal systems in the Pontiac Subprovince, leading either to the formation of "new" ore deposits like the Wright Mine, or to the remobilization of Archean mineralizations like the Lorraine and Patry deposits. Variations of the Pb isotopic composition and $\mu_1$ values between these deposits suggest a local derivation for Pb. For example, the large variation in the $^{207}Pb/^{204}Pb$ values for galena from the Wright Mine and the Proterozoic Pb-Ag veins, can only be explained by different sources of Pb, such as the metasedimentary rocks of the Cobalt Group for the more radiogenic component and the underlying volcanic rocks of the BB belt for the less radiogenic one.

A similar situation may have occurred at the Patry prospect. In fact, this deposit may have undergone more than one hydrothermal event as suggested by the distribution of the data points in the $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram (Fig. 3). The younger Pb-Pb age of 2050±48 Ma obtained from the sulfide minerals when all the data are included, compared to the age of 2172±17 Ma obtained when the two most radiogenic leachates are omitted, may be interpreted as two distinct perturbations of the U-Pb system. Alternatively, the age difference may be determined by the somewhat later closure of the U-Pb system of the more unstable mineral phases (*e.g.* Cumming and Krstic, 1991). However, the fact that the MSDW is considerably lower for the oldest isochron, and that the radiogenic leachates fall under this isochron, leads us to prefer the hypothesis of distinct hydrothermal phases. The age of the main remobilization is 2172 Ma but the age of the following one remains unknown, since a regression line including the radiogenic leachates is not an isochron. The $\mu_1$ value of 7.3, calculated for the Patry mineralization, is undoubtly too low to represent the mantle composition. The only way to explain this value is to invoke the recycling by hydrothermal fluids of U-poor minerals already present in the the crust. Pre-existing Archean sulfides within the tonalite would be appropriate candidates, as "unaltered" pyrite in the Kerr Adisson Ni-Cu prospect yielded time-integrated $^{238}U/^{204}Pb$ ratios as low as 3.

*Heat sources*

Early Proterozoic magmatic activity in the area is represented by the emplacement of the Nipissing and Preissac diabase dykes, dated by U-Pb between 2165 Ma and 2220 Ma (Corfu and Andrews, 1986; Buchan et al., 1991). Figure 6 shows the age of the BB deposits in comparison with the age of: (1) BB volcanism (Machado et al,. 1992); (2) early Proterozoic dykes (Corfu and Andrews, 1986; Hanes et al., 1989; Buchan et al., 1991); and (3) Cobalt Pb-Ag veins (Franklin et al., 1983). This diagram shows that the emplacement of the dykes is coeval with the formation and the remobilization of ore deposits. In addition, the 2219 Ma rutile found in the mineralized Nipissing diabase from the Castle Mine at Gowganda, Ontario, led Corfu and Andrews (1986) to invoke a possible genetic link with the silver-sulpharsenide deposits. The emplacement of the dykes could have supplied local heat sources leading to the establishment of small hydrothermal systems, resulting in ore formation in the Early Proterozoic.

## Conclusions

The Pb isotopic study of minerals from ore deposits of the late Archean Baby-Belleterre greenstone belt yielded unexpected results. Three mineralizations out of four have isotopic compositions compatible with a Proterozoic but not an Archean age. The Kerr Adisson Ni-Cu prospect is the only one that preserved its Archean signature. The age of 2694±30 Ma obtained from this deposit is compatible with the range of ages for volcanic rocks of the belt. The mineralization has not been affected by the surrounding intrusions of radiogenic post-volcanic plutons, yielding a low $\mu_1$ value of 7.8, similar to the komatiites of Abitibi. These data support the hypothesis that the BB supracrustal rocks may by a klippe of Abitibi belt on the Pontiac.

Silicates and sulfides from the Patry deposit have Pb-Pb ages of 2736±38 Ma and 2172±17 Ma, respectively. The low $\mu_1$ values calculated for the sulfides suggests that they are the product of a remobilization of pre-existing Archean U-poor mineral phases. Minerals from the Lorraine mine yield an age of 2.0±0.2 Ga, but the restricted range in compositions makes the error very large. When regressed with galena from the Wright mine, the data yield an age of 2210±40 Ma. The significance of this age is however disputable because mineralizing fluids of each deposit may have had different isotopic compositions.

The emplacement of Early Proterozoic diabase dykes in the area may have supplied the heat necessary to generate local hydrothermal systems, leading to the formation and remobilization of ore deposits in the BB greenstone belt.

## Acknowledgments

The authors are grateful to the financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Fonds pour la Formation des Chercheurs et l'Aide à la Recherche (FCAR) of Quebec. We are thankful to M. Rive for sample donation, to S.J. Barnes for her comments and to a journal reviewer for his report on the manuscript. Laboratory costs at GEOTOP are supported by infrastructure grants from NSERC and FCAR. LITHOPROBE Contribution No. 414.

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## Figure captions

Fig. 1. Schematic geological map of the Baby-Belleterre greenstone belt modified from Rive et al. (1990), in which appear the studied localities.

Fig. 2. (a) $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram showing data from the Kerr Adisson prospect and for K-feldspar from the adjacent Belleterre-Fugerville tonalite (Carignan et al., 1992). (b) $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram with reference lines of equal Th/U ratios of 3.8 and 0.75 passing through the K-feldspar residues of the tonalite.

Fig. 3. $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram showing data from the Patry Cu prospect. Plagioclase and K-feldspar (squares) from the mineralized tonalite yield an age of 2736±38 Ma. The sulfides (circles) define a younger age of 2050±48 Ma. An age of 2172±17 Ma is obtained for the sulfides when the two most radiogenic leachates (open circles) are omitted in the regression.

Fig. 4. $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram showing the composition of magnetite (open circles) and pyrrhotite (filled circles) from the Lorraine Mine.

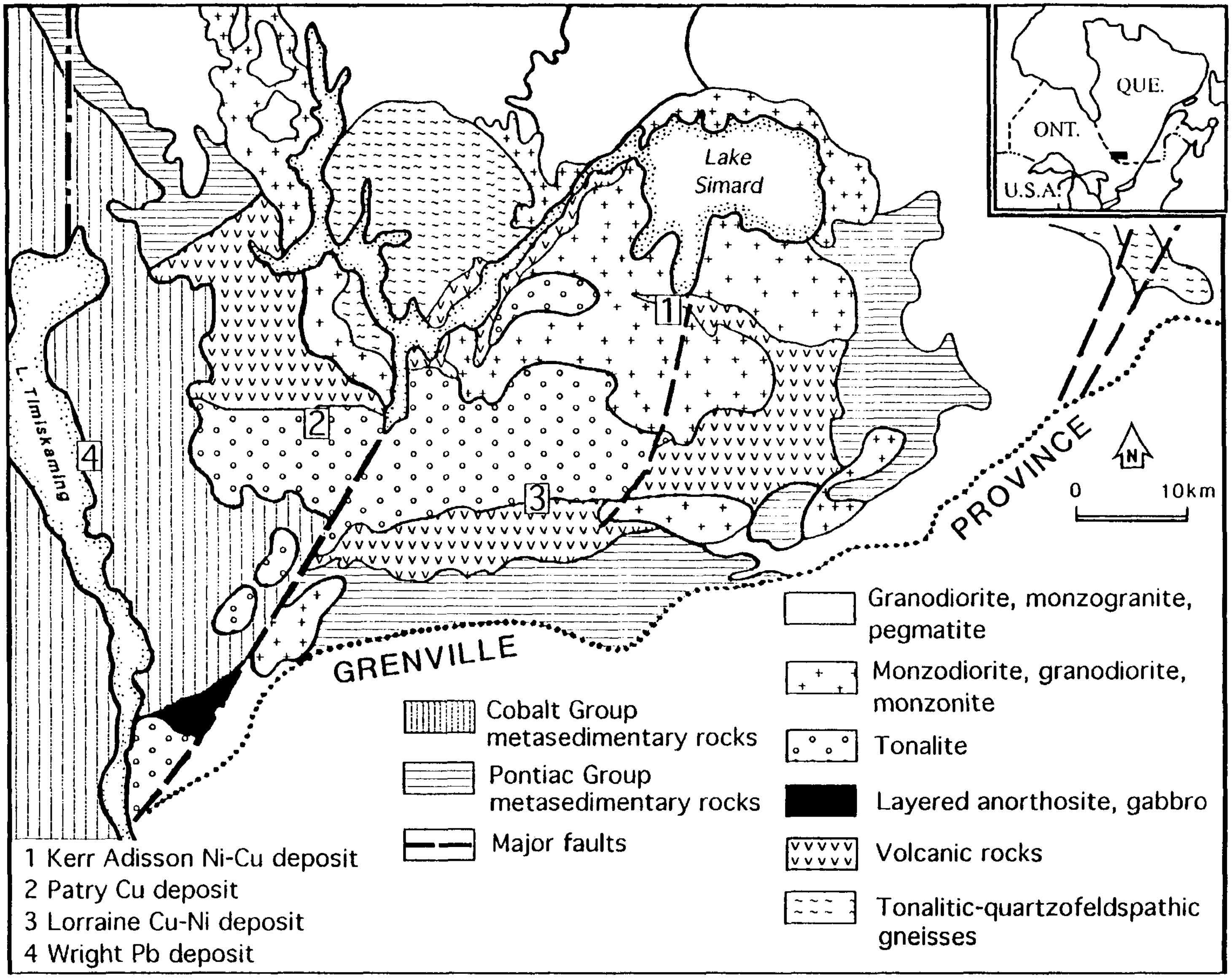
Fig. 5. (a) $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram showing the composition of galena (filled circles) and carbonates (open circles) from the Wright Mine and of galena from Proterozoic Pb-Ag veins (squares) in the Cobalt metasedimentary rocks (Franklin et al., 1983) with their $2\sigma$ error bars. (b) $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram sowing the results on minerals from the Lorraine and Wright deposits.

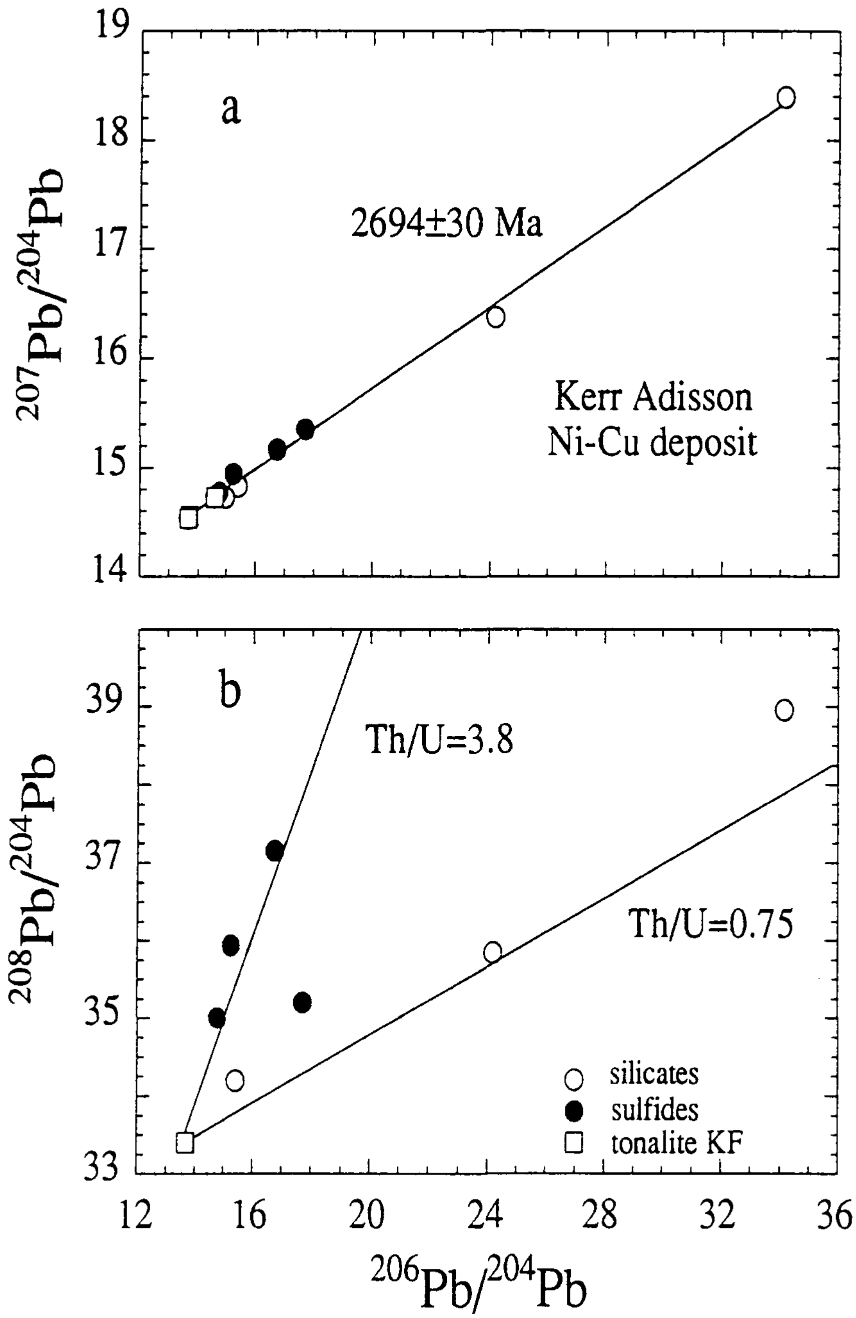
Fig. 6. Diagram comparing the age of: (1) BB belt mineralizations; (2) BB belt volcanic rocks (Machado et al., 1992); (3) Cobalt Pb-Ag veins (Franklin et al., 1983); and (4) early Proterozoic dykes (Corfu and Andrews, 1986; Hanes et al., 1989; Buchan et al., 1991).

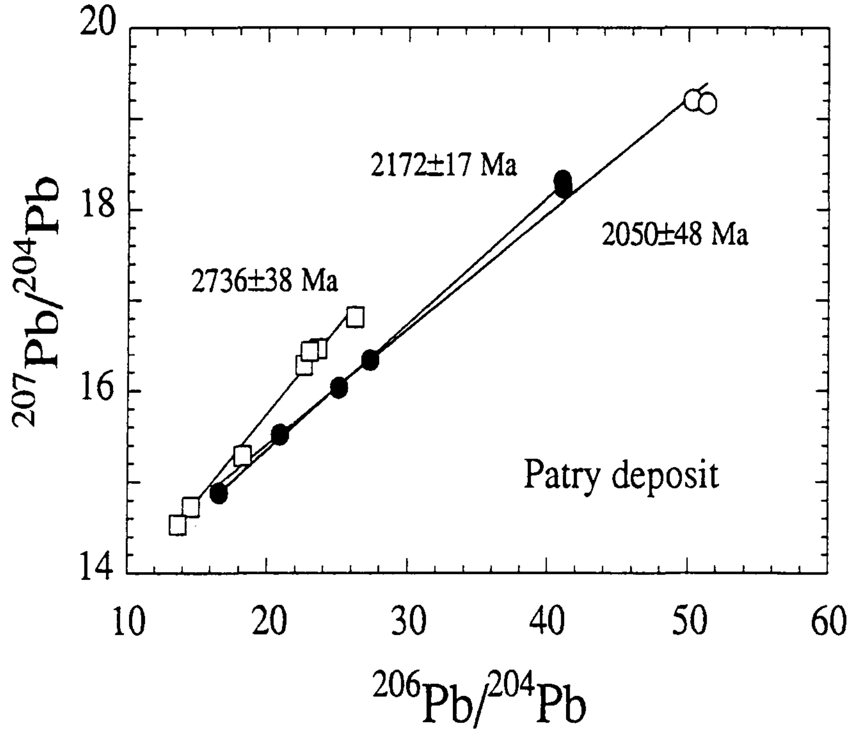
Table 1. Pb isotopic results on ore minerals from the BB greenstone belt.

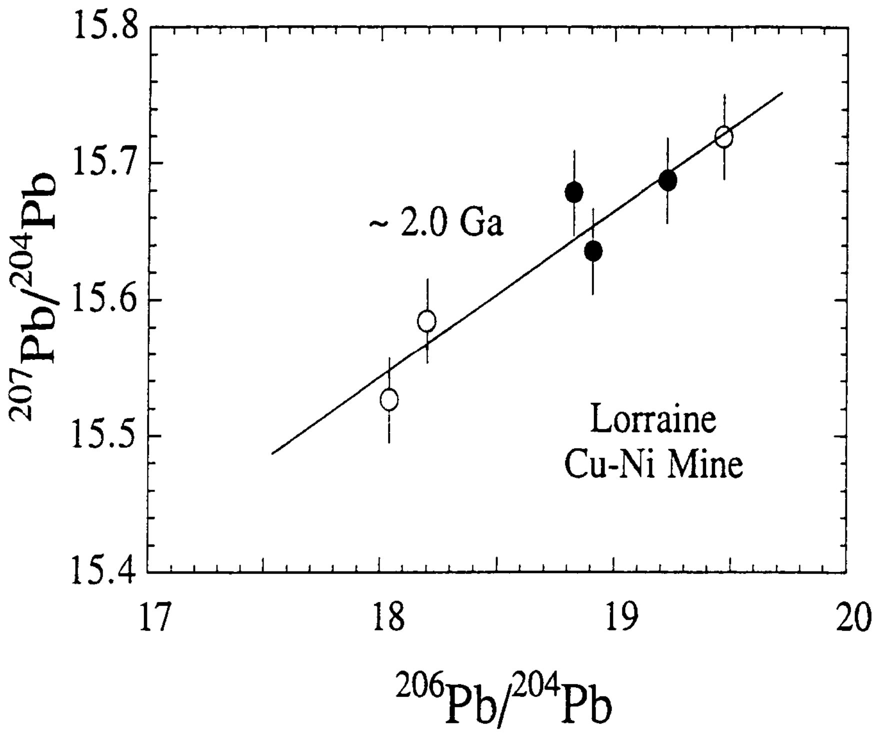
| Deposit | Sample | Acid leach | $^{206}Pb/^{204}Pb$ | $^{207}Pb/^{204}Pb$ | $^{208}Pb/^{204}Pb$ |
|---|---|---|---|---|---|
| Kerr | Pt/1 B | | 17.710 | 15.349 | 35.199 |
| Adisson | Pt/2 B | | 16.744 | 15.166 | 37.153 |
| | Py/1 B | | 15.250 | 14.943 | 35.931 |
| | Py/2 B | | 14.782 | 14.773 | 35.001 |
| | Pl L | HF-HBr | 24.193 | 16.372 | 35.844 |
| | Pl R | | 34.168 | 18.391 | 38.954 |
| | Amp L | HF-HBr | 14.984 | 14.726 | - |
| | Amp R | | 15.437 | 14.826 | 34.191 |
| Patry | Pl/1 L | HF-HBr | 22.980 | 16.429 | 39.943 |
| | Pl/1 R | | 22.571 | 16.278 | 38.557 |
| | Pl/2 L | HF-HBr | 26.221 | 16.812 | 41.909 |
| | Pl/3 L | HF-HBr | 23.527 | 16.461 | 40.589 |
| | Pl/3 R | | 18.403 | 15.396 | 36.009 |
| | Py B | | 25.080 | 16.030 | 42.512 |
| | Py L | 6N HCl | 42.042 | 18.311 | 54.972 |
| | Py R | | 20.925 | 15.516 | 39.054 |
| | Py-Cp/1 B | | 41.083 | 18.241 | 52.150 |
| | Py-Cp/1 L | $CH_3COOH$ | 50.333 | 19.198 | 57.750 |
| | Py-Cp/1 R | | 27.315 | 16.331 | 42.531 |
| | Py-Cp/2 L | 6N HCl | 51.354 | 19.158 | 59.275 |
| | Py-Cp/2 R | | 16.645 | 14.873 | 35.152 |
| Lorraine | Mg L1 | 6N HCl | 18.200 | 15.584 | 38.159 |
| | Mg L2 | 6N HCl | 18.041 | 15.526 | 37.704 |
| | Mg R | | 19.468 | 15.719 | 38.264 |
| | Pt L1 | $CH_3COOH$ | 18.824 | 15.679 | 38.468 |
| | Pt L2 | 1N HBr | 18.908 | 15.635 | 38.247 |
| | Pt R | | 19.227 | 15.687 | 38.429 |
| Wright | Gn-1 B | | 14.675 | 15.068 | 34.212 |
| | Gn-2 B | | 14.685 | 15.079 | 34.256 |
| | Gn-3 B | | 14.668 | 15.052 | 34.185 |
| | Ca-1 B | | 14.831 | 15.114 | - |
| | Ca-2 L | $CH_3COOH$ | 14.749 | 15.185 | 34.751 |
| | Ca-2 R | | 14.716 | 15.112 | 34.333 |

Amp: amphibole; Mg: magnetite; Cp: chalcopyrite; Gn: galena; Ca: carbonate; Pt: pyrrhotite; Py: pyrite; Pl: plagioclase; B: bulk; L: leachate; R: residue.
1, 2 and 3 are different aliquots of the same sample.

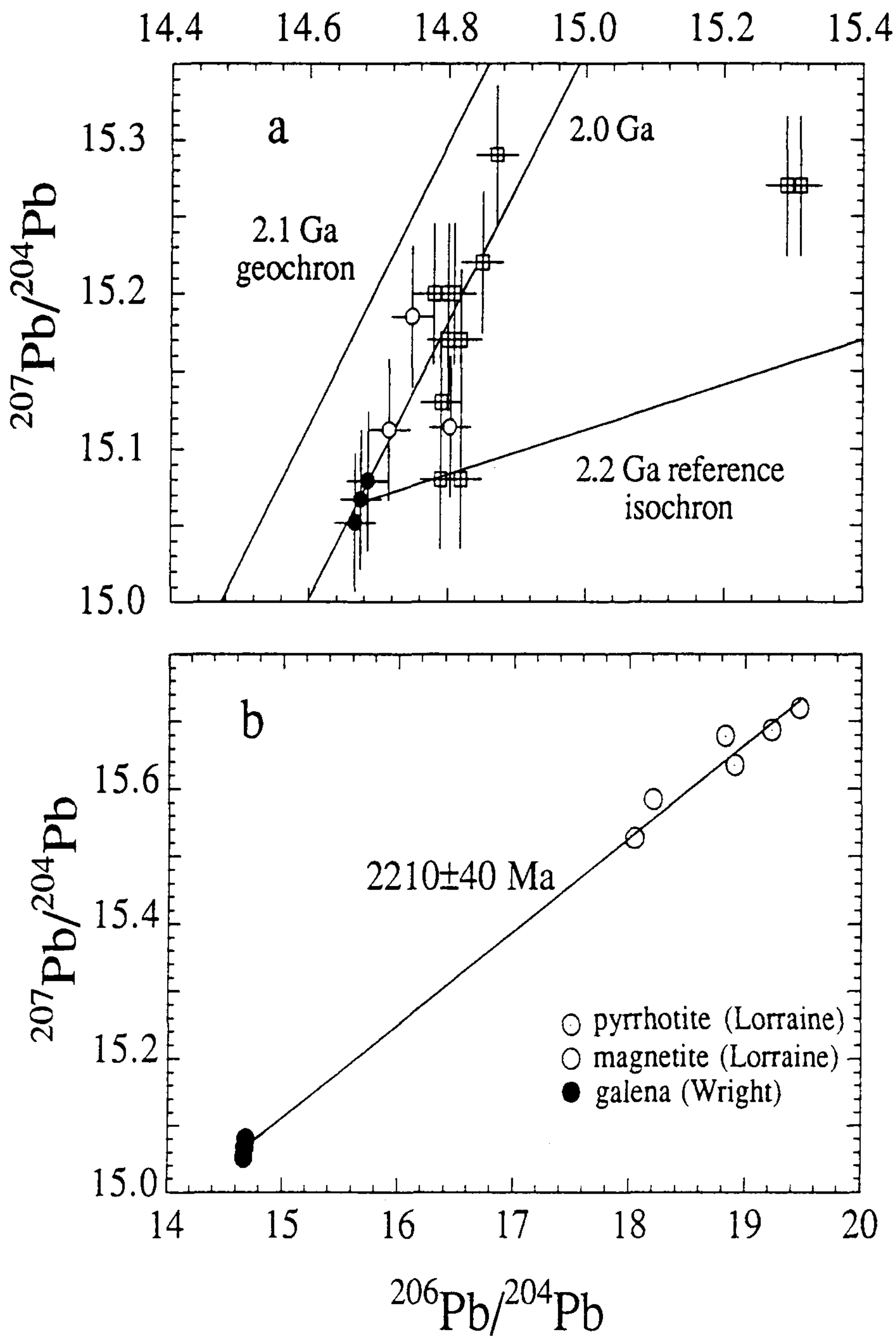

QUE.
ONT.
U.S.A.
Lake Simard
L. Timiskaming
1
2
3
4
GRENVILLE
PROVINCE
N
0
10km
Cobalt Group metasedimentary rocks
Pontiac Group metasedimentary rocks
Major faults
Granodiorite, monzogranite, pegmatite
Monzodiorite, granodiorite, monzonite
Tonalite
Layered anorthosite, gabbro
Volcanic rocks
Tonalitic-quartzofeldspathic gneisses
1 Kerr Adisson Ni-Cu deposit
2 Patry Cu deposit
3 Lorraine Cu-Ni deposit
4 Wright Pb deposit

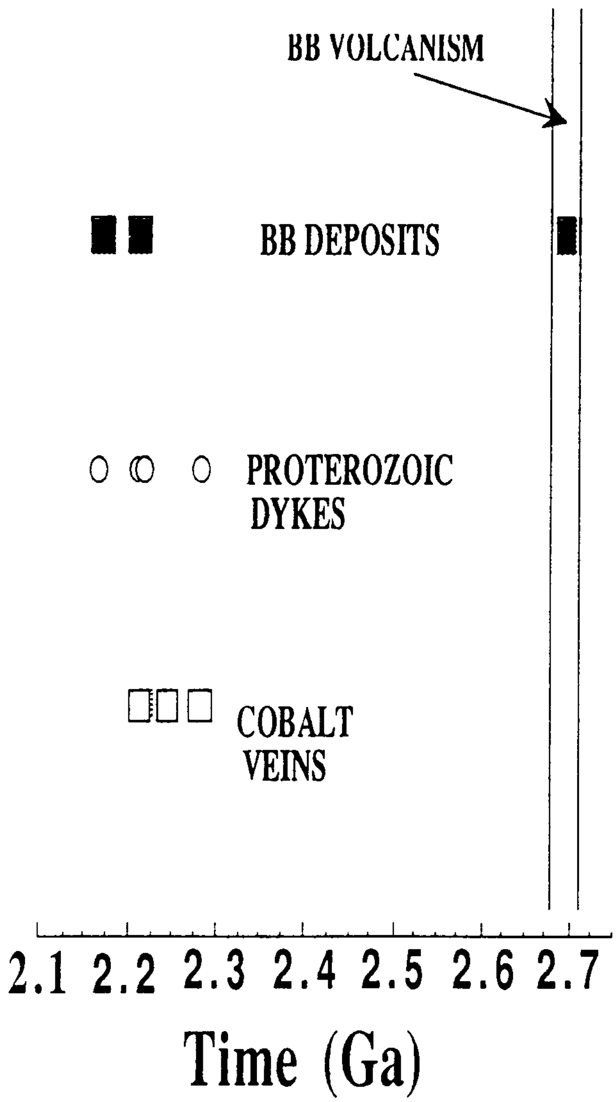

a
2694±30 Ma
Kerr Adisson
Ni-Cu deposit
$^{207}Pb/^{204}Pb$
b
Th/U=3.8
Th/U=0.75
silicates
sulfides
tonalite KF
$^{208}Pb/^{204}Pb$
$^{206}Pb/^{204}Pb$


2172±17 Ma
2050±48 Ma
2736±38 Ma
Patry deposit
20
18
16
14
10
20
30
40
50
60
$^{207}Pb/^{204}Pb$
$^{206}Pb/^{204}Pb$



15.8
15.7
15.6
15.5
15.4
$^{207}Pb/^{204}Pb$
~ 2.0 Ga
Lorraine
Cu-Ni Mine
17
18
19
20
$^{206}Pb/^{204}Pb$


14.4
14.6
14.8
15.0
15.2
15.4
a
2.0 Ga
2.1 Ga
geochron
2.2 Ga reference
isochron
15.3
15.2
15.1
15.0
$^{207}Pb/^{204}Pb$
b
15.6
15.4
15.2
15.0
2210±40 Ma
pyrrhotite (Lorraine)
magnetite (Lorraine)
galena (Wright)
14
15
16
17
18
19
20
$^{206}Pb/^{204}Pb$


BB VOLCANISM
BB DEPOSITS
PROTEROZOIC DYKES
COBALT VEINS
2.1 2.2 2.3 2.4 2.5 2.6 2.7
Time (Ga)

# CONCLUSIONS

L'étude des isotopes du Pb de différents minéraux provenant de gîtes de molybdène, or, cuivre, nickel et plomb ainsi que des roches encaissantes dans les provinces du Supérieur et de Grenville a permis de définir plusieurs paramètres utiles à l'élaboration de modèles métallogéniques. Ces paramètres sont: (1) la composition isotopique des réservoirs potentiels, (2) l'âge absolu des minéralisations, (3) la région-source des métaux, (4) la caractérisation géochimique des gîtes, et (5) la détection et la datation de processus de remobilisation des minéraux porteurs du minerai.

Les roches granitoïdes des sous-provinces de l'Abitibi et du Pontiac possèdent une grande variété de compositions isotopiques initiales du Pb. La composition des gneiss démontre la présence de réservoirs isotopiques très radiogéniques à l'Archéen dans la sous-province de Pontiac ainsi que le long de sa frontière sud avec la zone tectonique du front de Grenville. Les tonalites, trondhjémites, diorites, monzodiorites et granodiorites, mises en place entre 2.72 et 2.69 Ga, possèdent des compositions relativement homogènes, caractéristiques de matériel juvénile. Les monzonites mises en place à la fin du cycle volcanique (2685 Ma) présentent aussi des compositions homogènes mais proviennent de réservoirs plus radiogéniques que les plutons précédents. Les roches granitoïdes post-tectoniques, mises en place entre 2.68 et 2.64 Ga sont les plus radiogéniques, témoignant de la fusion de segments de croûte évoluée. La différence de composition isotopique entre les granites radiogéniques de l'Abitibi et ceux du Pontiac peut s'expliquer par une différence d'âge entre les "socles" remobilisés. Des âges minima de *ca.* 2.8 Ga et 3.0 Ga ont été estimés pour les socles de l'Abitibi et du Pontiac, indiquant que les deux sous-provinces représentent des segments de croûte distincts juxtaposés tectoniquement.

La méthode de lessivage à l'acide, appliquée à différents minéraux provenant de concentrations métallifères des provinces du Supérieur et de Grenville, s'est avérée efficace pour obtenir un étalement de points dans le diagramme isochrone du Pb à partir d'un seul cristal. Les âges Pb-Pb obtenus par cette méthode sont généralement en accord avec la géochronologie connue des régions étudiées. La plupart des âges Pb-Pb obtenus pour les gîtes d'or et de molybdène de l'Abitibi se placent dans la fourchette d'âges déjà définie par d'autres géochronomètres (U-Pb, Ar-Ar, Sm-Nd) sur différents minéraux des gîtes d'or du sud de l'Abitibi situés le long de la faille Cadillac-Larder-Lake: 2630 à 2550 Ma. L'évidence d'activité hydrothermale dans cette fourchette d'âges à plus de 50 km au nord de cette faille (gîte de Launay) supporte l'idée d'un métamorphisme régional à cette époque.

La composition isotopique des zones minéralisées en molybdène et en or du sud de l'Abitibi indique différentes sources de Pb. La composition isotopique des feldspaths potassiques provenant de la zone minéralisée de Launay ainsi que celle du quartz de Silidor sont nettement plus radiogéniques que celle des feldspaths provenant des roches encaissant la minéralisation, suggérant des sources de Pb distinctes. Les données isotopiques du Pb pour les gîtes d'or de la province du Supérieur, provenant de notre étude et de la littérature, sont comparées aux compositions isotopiques initiales de Pb des granitoïdes des sous-provinces de l'Abitibi et du Pontiac. Les veines de quartz aurifères encaissées dans les assemblages volcano-sédimentaires possèdent des compositions variées couvrant toute la gamme des compositions, du domaine mantellique au domaine crustal. Les minéralisations aurifères contenues à l'intérieur des roches granitoïdes possèdent géneralement des compositions plus radiogéniques, témoignant d'une source à caractère plutôt crustale. La majorité des gîtes de molybdène possèdent également des compositions isotopiques compatibles avec une origine crustale.

Certains gîtes de molybdène des sous-provinces de Wabigoon et de l'Abitibi ont livré des âges Pb-Pb protérozoïques, interprétés comme datant une remobilisation du sulfure. Ces âges correspondent bien avec des événements thermiques post-archéens déjà connus dans la province du Supérieur. Il s'agit de la mise en place des dykes de Matachewan à ca. 2450 Ma, des dykes de Fort Frances, Preissac et Nipissing de 2.2 à 2.1 Ga ainsi que de l'altération régionale des dykes de Nipissing, entre 1.8 et 1.7 Ga. Le bilan géochimique indique une perte de 30 à 40% de l'uranium relative au Pb lors de ces perturbations. Tous les échantillons de molybdénite montrent aujourd'hui des déficits de 50 à 99% en uranium relatifs au Pb.

Cette situation implique que tous les âges Pb-Pb sur les cristaux de molybdénite sont des âges maxima. Les sulfures et oxydes provenant de trois dépôts minéralisés de la ceinture volcanique de Baby-Belleterre dans le sud du Pontiac ont également livré des âges Pb-Pb protérozoïques entre 2.1 et 2.2 Ga, correspondant aux âges de mise en place des dykes de Nipissing et de Preissac.

Les événements thermiques ayant engendré la formation des dykes protérozoïques a aussi généré la circulation de fluides hydrothermaux, lesquels sont responsables de la remobilisation et de la formation de gîtes de Mo, Cu, Ni et Pb dans la province du Supérieur pendant le Protérozoïque. La capacité d'identifier ces remobilisations est d'une grande importance en métallogénie car la connaissance d'une redistribution des sulfures archéens au Protérozoïque peut influencer l'interprétation de données géochimiques et isotopiques sur les roches minéralisées.