

Zeitschrift: Schweizerische mineralogische und petrographische Mitteilungen =
Bulletin suisse de minéralogie et pétrographie

Band: 77 (1997)

Heft: 1

Artikel: Pb stepwise leaching (PbSL) dating of garnet-addressing the inclusion
problem

Autor: Schaller, Mirjam / Steiner, Oliver / Studer, Ivan

DOI: <https://doi.org/10.5169/seals-58473>

Nutzungsbedingungen

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. [Mehr erfahren](#)

Conditions d'utilisation

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. [En savoir plus](#)

Terms of use

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. [Find out more](#)

Download PDF: 30.04.2026

ETH-Bibliothek Zürich, E-Periodica, <https://www.e-periodica.ch>

Pb stepwise leaching (PbSL) dating of garnet-addressing the inclusion problem

by *Mirjam Schaller, Oliver Steiner, Ivan Studer, Robert Frei and Jan D. Kramers¹*

Abstract

The problem of monazite and zircon inclusions for garnet geochronology has long been recognized. Both phases occur as (sub)microscopic inclusions in the majority of metamorphic garnets, and their presence can massively influence the budgets of U, Th, Pb and other elements and therefore may strongly affect – if not dominate – the apparent age obtained for the host mineral. Special care has to be taken if such inclusions were formed during earlier events, as they are often highly retentive for U, Th and Pb, and bulk garnet dating will give geologically meaningless mixing ages. To assess this critical issue we have selected three garnets from different metamorphic terrains on which we performed Pb stepwise leaching (PbSL). We demonstrate that PbSL is potentially successful (i) to detect micro-inclusions of monazite and zircon in garnet by analyzing the step leaching Pb isotope spectra in the thorogenic vs uranogenic data array, (ii) to selectively and quantitatively remove monazite-derived Pb from sufficiently fine-grained host garnet splits and therefore to obtain monazite-free Pb–Pb isochron ages of the host garnet, (iii) to assess whether or not inclusions were in isotope equilibrium with their host as this crystallized, and subsequently (iv) to constrain the approximate age of the interfering monazite and zircon inclusions.

Keywords: Pb isotopes, geochronology, Pb stepwise leaching, garnet, monazite, zircon.

Introduction

The interest in dating rock-forming minerals, as a geologically important alternative to accessory phases, has greatly increased in the past few years. This is because direct age information on a metamorphic and/or tectonic event forming or deforming a paragenesis can generally be obtained only from common silicates. Garnet is one of these minerals, and its importance for constraining metamorphic conditions is well known. Bulk garnet U–Pb dating has been successfully performed by many workers (e.g., MEZGER et al., 1989; BURTON and O'NIONS, 1991; LANZIROTTI and HANSON, 1995, and others) and these data were used to calculate P–T–t information. Also, garnet-bearing metamorphic parageneses were assessed by the conventional two-phase (i.e., garnet-feldspar) Pb–Pb dating technique (e.g., BARTON et al., 1994; HOLZER et al., in press; KAMBER et al., 1995, and many others), with the aim to obtain age information on medium to high grade metamorphic events. Except in case where the

parent/daughter ratio in a mineral is very high (i.e., if the proportion of initial Pb relative to radiogenically produced Pb is negligibly small), the latter technique relies on the assumption that isotope equilibrium between the two phases at the time of their formation was attained. Unless otherwise established, this assumption remains uncontrolled and can lead to erroneous and geologically uncertain age constraints (c.f., HOLZER et al., in press; KAMBER et al., 1995).

U–Pb dating of garnet is usually difficult due to its low concentration of uranium. Further, garnet often contains inclusions of Th–U-rich phases such as monazite and zircon. Bulk "garnet" data, and consequently also "two phase" dating techniques, therefore rely on the assumption that these inclusions crystallized at the time of garnet growth and/or that the inclusions were in isotope equilibrium with the host mineral / whole rock at the time of formation of garnet (e.g., MEZGER et al., 1989). Since such inclusions may place serious limitations on the use of U–Pb bulk garnet geochronology, aliquots of sample material to

¹ Gruppe Isotopengeologie, Mineralogisch-Petrographisches Institut, Universität Bern, Erlachstr. 9a, CH-3012 Bern, Switzerland.

date have been previously "screened" for inclusions by utilizing several methods, e.g., scanning electron microscopy (SEM, MEZGER et al., 1989), fission tracks (DEWOLF et al., 1996), and secondary ionization mass spectrometry (SIMS, VANCE et al., 1991; DEWOLF et al., 1994). These techniques have the disadvantage that they are destructive and that therefore they cannot actually be applied to the sample aliquot from which age data are obtained.

Pb stepwise leaching (PbSL) not only enables single mineral Pb–Pb dating of many rock-forming minerals (FREI and KAMBER, 1995; FREI et al., 1995; FREI and PETTKE, 1996; FREI et al., 1997) but it also offers the opportunity to evaluate the extent of inter and intra-mineral isotope equilibrium (e.g., FREI, 1996; NÄGLER et al., 1995b; NÄGLER et al., 1996). In a number of studies PbSL was successfully applied to garnet (e.g., FREI and KAMBER, 1995; FREI, 1995; BLENKINSOP and FREI, in press; BUICK et al., *subm.*). In all these studies it became obvious that certain acid leach steps were either dominated by highly thorogenic relative to uranogenic Pb compositions (or vice versa), revealing the influence of (sub)microscopic inclusions of either monazite and/or zircon.

In order to clearly distinguish Pb components originating from different phases, it would be advantageous to know the U/Th characteristics of every individual one. However the U–Th partition coefficients and the concentrations of these elements in the majority of rock-forming minerals, and specifically of garnet, are not well constrained. Partition coefficients (K_d values) for the most abundant accessories monazite and zircon (which are frequently included in garnet) are better known. U tends to go with heavy rare earth elements (HREE) and Th with the light ones (LREE), suggesting that the REE K_d 's are generally a good approximation for the partitioning of Th and U. LREE's are highly incompatible in the zircon lattice, and therefore very high U/Th ratios are characteristic of this mineral. Monazite, in contrary, because of its ability to incorporate LREE's, shows generally very high Th/U ratios. With respect to garnet one would expect to observe a wide range of U/Th ratios, dependent on its chemical composition (e.g., DEWOLF et al., 1996). Due to the similar ionic radii of Th and Ca, and of U and Fe, it is likely that in garnets with a significant grossularite component Ca can be easily substituted by Th, whereas almandine rich garnets would preferably incorporate U.

In order to better understand the role and effects of inclusions in garnet for geochronological applications we have performed PbSL on three garnet samples from metamorphic rocks in differ-

ent geological settings. The variation of observed Pb isotope characteristics of the leach spectra presented in this paper is considered to depict the most commonly encountered host mineral-contaminant patterns. The aim in this study is to show a variety of leaching spectra and to deduce implications for the kind of U and Th rich inclusions in garnet. Furthermore, the most important question with respect to possible age constraints which can be drawn from stepwise leaching of "garnet", i.e., whether or not inclusions were in isotope equilibrium with the host at the time of its formation or retained older ages, is addressed and potential directions for the interpretation of PbSL data are given. The three characteristic leaching patterns may serve as reference spectra and could be of help for the interpretation of further age data from this rock-forming mineral.

Analytical techniques

Garnet separates were obtained from crushed (< 250 μm) whole rock hand specimens using standard magnetic separation and heavy liquid techniques. The final separates were hand picked under a high-power binocular microscope and were optically assessed as being pure. Great care was taken to avoid inclusions of high- μ accessory phases. Pb stepwise leaching (PbSL) technique followed that of FREI and KAMBER (1995) with modifications of leaching intervals (see Tab. 1). The separates were ultrasonically washed in twice distilled water and subsequently 90–200 mg were treated in 7 ml Savillex® screw-top beakers. Between steps the leach solutions were decanted (partly after centrifuging) and then dried on a hot plate. After conversion to the chloride form with 1 ml of 6 N HCl and renewed subsequent drying, Pb was separated using a conventional HCl–HBr anion exchange procedure, contributing a blank of less than 130 pg. The Pb was loaded on single Re-filaments and measured on a VG Sector® mass spectrometer running in static mode. Pb isotope ratios were corrected for fractionation using the values obtained from repetitive NBS SRM 981 runs under similar operating conditions ($0.068 \pm 18\%/AMU$, $n = 84$). Error correlations were calculated using the method of LUDWIG (1988). Errors assigned to the isochrons are two standard deviations (2σ).

Sample material

SAMPLE OS-1178

Sample OS-1178 is a garnet-bearing biotite-quartz-plagioclase gneiss from the Precambrian

crystalline basement of Salalah, Dhofar area, Sultanate of Oman (WÜRSTEN, 1994). It belongs to the so-called Juffa Group, a high-grade metasedimentary sequence possibly deposited in a fore arc basin. The Juffa Group is tectonically juxtaposed with a province of calc-alkaline magmatic and migmatitic rocks earlier known as the Sadh Complex (e.g., WÜRSTEN, 1994) which is interpreted as a high-grade metamorphic accretionary wedge. The rocks exposed in the Salalah area are considered to have been produced in a typical island arc setting in which calc-alkaline melts were generated above an intra-oceanic subduction zone. They were accreted against the Arabian Nubian Shield in the late Precambrian in an event apparently involving considerable crustal thickening followed by uplift. On the basis of textural differences in thin sections two generations of garnets are described by WÜRSTEN (1994). Electron microprobe analyses however did not reveal differences in their chemical compositions. The garnets are composed of the following endmembers: ~ 66% almandine, ~ 16% spessartine, and ~ 12% pyrope with minor andradite and grossular components (WÜRSTEN, 1994). Furthermore, garnets from sample OS-1178 are homogeneous with respect to their main elements. WÜRSTEN (1994) reports quantitative P-T estimates from quartz-plagioclase-garnet-biotite-muscovite-sillimanite equilibrium parageneses in several rocks from the Juffa Group in the range of 650–730 °C at pressures between 6.5–8.5 kbars. WÜRSTEN (1994) reports a biotite-whole rock Rb–Sr age of 820 ± 7 Ma with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.7044 ± 0.0004 for sample OS-1178. Conventional U–Pb dating of zircon from this sample yielded an upper intercept age of 822 ± 12 Ma (WÜRSTEN, 1994). Taking into consideration that the zircons show core-rim relationships, this age is interpreted as a minimum age for a possible precursor and a maximum age for the migmatization. A remarkable feature of the magmatic-metamorphic basement of the Salalah area is that all ages cluster very closely around 800 Ma and no indications of significantly older ages have been found even in zircon populations displaying cores and rims (WÜRSTEN, 1994; SCHÖNBERG, 1996, new unpublished data). For this reason it is unlikely that garnet from sample OS-1178 contains older inclusions and therefore could potentially represent a geochronologically simple case.

SAMPLE 95/427

This metapelitic mylonite is part of a less mylonitized lens in the Palala Shear Zone in the Limpopo Belt (South Africa). The 15 km wide,

largely mylonitic Palala strike slip zone defines the suture zone between the Limpopo Central Zone to the North and the Bushveld Complex to the South. Within the Palala Shear Zone granulite facies gneisses have been mylonitized at low grade conditions after the emplacement of the Bushveld Igneous Complex (< 2060 Ma). Archean granulite facies metamorphism has been identified in the Southern Marginal Zone at 2.65–2.7 Ga and is also suggested in the Central Zone (e.g., VAN REENEN et al., 1992, and references therein; BARTON et al., 1994, and references therein). High-grade metamorphism overprinted the Central Zone at 2.0 Ga (BARTON et al., 1994; HOLZER et al., in press). A metapelitic mylonite of the Palala Shear Zone similar to sample 95/427 yielded a two-point garnet-whole rock Pb–Pb age of 2601 ± 26 Ma (KAMBER, pers. comm.) suggesting that the high grade metamorphism here was Archean (with the obvious reservations applying to bulk garnet dating). The studied metapelitic mylonite consists of hypersthene and garnet porphyroblasts in a quartz- and plagioclase-dominated matrix which contains tiny biotite flakes. Garnet contains microscopic inclusions of biotite, plagioclase, K-feldspar, quartz and an opaque mineral. Furthermore, garnet shows weak major element zoning. The core is composed of ~ 59% almandine, ~ 36% pyrope, ~ 3% andradite and minor spessartine endmember components. The rim is enriched in the almandine, but slightly depleted in the pyrope endmember (almandine ~ 64%, pyrope ~ 32%, andradite ~ 4%). Such zoning usually results from decompression reactions. With the documentation of both Archean (2.6 Ga) and Proterozoic (2.0 Ga) high grade metamorphic events in the area, this sample could have a complicated history and multiple or mixed apparent ages would not be unexpected.

SAMPLE LF-1

This sample is an amphibolite from the Black Hills (South Dakota). Early Proterozoic sedimentary rocks in the Black Hills were tectonically buried during a late phase of the Trans Hudsonian orogeny and then uplifted (HOLM et al., *subm.*). Garnet occurs as coarse grained euhedral grains (up to 2–3 cm in diameter). Inclusions are abundant: graphite, ilmenite, ± biotite and ± chlorite. From field observations the garnets were interpreted to have formed in the thermal alteration halo of the post tectonic Harney Peak granite/pegmatite complex dated at 1715–1702 Ma (REDDEN et al., 1990; KROGSTAD and WALKER, 1994), rather than to have crystallized during

Tab. 1 PbSL data of three different garnets

sample	mineral [†]	acid [§]	time	code#	²⁰⁶ Pb/ ²⁰⁴ Pb	± 2 σ ⁺	²⁰⁷ Pb/ ²⁰⁴ Pb	± 2 σ ⁺	²⁰⁸ Pb/ ²⁰⁴ Pb	± 2 σ ⁺	r ₁ **	r ₂ ††
OS-1178	grt	mix	15'	[1]	18.383	0.027	15.542	0.024	44.848	0.070	0.988	0.980
OS-1178	grt	8N HBr	8h	[2]	20.777	0.029	15.695	0.022	65.803	0.096	0.980	0.976
OS-1178	grt	8N HBr	8h	[3]	116.661	0.548	22.026	0.104	835.443	3.945	0.993	0.997
OS-1178	grt	15N HNO ₃	16h	[4]	181.639	1.707	26.348	0.248	1297.919	12.213	0.999	0.999
OS-1178	grt	HF, residue	2d	[5]	24.031	0.082	15.900	0.055	44.370	0.153	0.990	0.992
95/427	grt	mix	15'	[1]	18.489	0.119	15.678	0.102	39.578	0.258	0.994	0.992
95/427	grt	4N HBr	4h	[2]	103.245	6.304	31.010	1.895	209.632	12.803	0.999	1.000
95/427	grt	8N HBr	13h	[3]	101.924	11.131	30.576	3.342	177.770	19.416	0.999	1.000
95/427	grt	15N HNO ₃	2d	[4]	25.231	1.303	16.827	0.871	44.834	2.316	0.998	1.000
95/427	grt	HF, residue a	4d	[5a]	31.191	1.611	18.037	0.937	39.463	2.043	0.995	0.998
95/427	grt	HF, residue b	6d	[5b]	52.495	0.691	21.539	0.286	39.741	0.529	0.992	0.990
95/427	grt	HF, residue c	10d	[5c]	39.618	0.378	19.356	0.186	38.773	0.372	0.993	0.997
LF-1	grt	mix	15'	[1]	37.833	0.593	17.908	0.282	47.475	0.746	0.996	0.999
LF-1	grt	4N HBr	3h	[2]	47.706	0.397	18.899	0.158	47.748	0.400	0.997	0.997
LF-1	grt	8N HBr	20h	[3]	63.236	5.143	20.190	1.646	39.706	3.230	0.998	1.000
LF-1	grt	15N HNO ₃	27h	[4]	18.668	0.191	15.661	0.162	38.122	0.394	0.993	0.994
LF-1	grt	HF, residue a	4d	[5a]	307.129	9.578	46.012	1.436	43.687	1.363	0.999	0.999
LF-1	grt	HF, residue b	6d	[5b]	260.953	35.029	40.918	5.496	44.210	5.938	0.999	0.999

† grt = garnet

§ mix = 1.5N HBr–2N HCl 12 : 1 mixture used in the first leach step

Step leaching codes according to table 1 (FREI and KAMBER, 1995; with slight modifications)

** r₁ = ²⁰⁶Pb/²⁰⁴Pb vs ²⁰⁷Pb/²⁰⁴Pb error correlation after Ludwig (1988)

†† r₂ = ²⁰⁶Pb/²⁰⁴Pb vs ²⁰⁸Pb/²⁰⁴Pb error correlation after Ludwig (1988)

+ Errors are two standard deviations absolute after Ludwig (1988)

earlier regional high-grade metamorphic conditions.

Results and discussion

The analytical results are given in table 1. In figures 1–3 the leaching spectra obtained by PbSL are presented in the form of uraniumogenic (²⁰⁷Pb/²⁰⁴Pb vs ²⁰⁶Pb/²⁰⁴Pb) and thorogenic (²⁰⁸Pb/²⁰⁴Pb vs ²⁰⁶Pb/²⁰⁴Pb) Pb isotope diagrams. These diagrams permit to discriminate between the release of both types of radiogenic Pb relative to common, i.e. primarily built-in Pb, in the sample garnets. In the following we want to discuss the three basically different PbSL spectra in the light of what they can tell us about the sample garnets and their implications for geochronology and genesis.

SAMPLE OS-1178

Lead measured from the step solutions of sample OS-1178 is increasingly radiogenic from step to step. The most primitive Pb (²⁰⁶Pb/²⁰⁴Pb ~18.4) was released by the HCl–HBr mixture during step [1], whereas the most radiogenic one (²⁰⁶Pb/²⁰⁴Pb ~180) was measured in the HNO₃-step [4]. The residual step [5] is again characterized by an un-

radiogenic value of ~24 which is in the range of values obtained from steps [1] and [2] (Tab. 1). All step leaching data define an isochron of 809 ± 17 Ma (MSWD = 0.16; Fig. 1a) in perfect agreement with the zircon and biotite ages of this sample. In the thorogenic diagram a near linear arrangement of data points is also indicated (Fig. 1b). The highly ²⁰⁶Pb/²⁰⁴Pb values of Pb released during steps [3] and [4] are matched by similarly high ²⁰⁸Pb/²⁰⁴Pb ratios. The only outlier in figure 1b is fraction 5, which shows a contribution of a phase with low Th/U ratio.

Sample OS-1178 yielded linear arrays in both the uraniumogenic and thorogenic diagrams. A linear arrangement of PbSL data points in the thorogenic diagram (i.e., thorogenic and uraniumogenic Pb release takes place at a more or less constant rate) implies that single phase garnet was leached, and that therefore the possible contribution of Pb from micro-inclusions to the leaching acids was insignificant in this case. However, the small offset of the residue from the line towards a slightly more uraniumogenic value in the ²⁰⁸Pb/²⁰⁴Pb vs ²⁰⁶Pb/²⁰⁴Pb diagram can be interpreted as resulting from a minor admixture of Pb from submicroscopic zircon inclusions which could only be attacked by HF in the final residual digestion. A similar case, in which subordinate zircon inclu-

sions could be traced only in the residue of a PbSL spectrum, has been reported previously by FREI et al. (1997) for titanite. It is suggested that in the case of garnet OS-1178 both U and Th were primarily incorporated into the structure at the time of formation of this garnet. Our PbSL isochron age is likely to pinpoint the crystallization age of garnet in the Juffa Group of the Salalah area.

SAMPLE 95/427

Leach spectra of sample 95/427 are plotted in figure 2a (uranogenic diagram) and 2b (thorogenic diagram), and the corresponding PbSL data are contained in table 1. The HCl-HBr mixture, similarly to sample OS-1178, recovered the most primitive Pb with $^{206}\text{Pb}/^{204}\text{Pb} \approx 18.5$. Nearly identical and very radiogenic Pb components ($^{206}\text{Pb}/^{204}\text{Pb} \approx 100$; $^{208}\text{Pb}/^{204}\text{Pb} \approx 210$, 178) were released during both strong HBr steps [2] and [3]. The high $^{208}\text{Pb}/^{204}\text{Pb}$ ratios are well correlated with the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. The successive leaching steps are less radiogenic, and only their uranium Pb isotope compositions increase again from step [4] to [5b]. The very last dissolution step [5c] yielded a Pb isotope composition which is between the two other HF-attacks. The very thorogenic Pb compositions likely signify the presence of submicroscopically small monazite inclusions ("monazite" trend in Fig. 2b). The contribution of Pb from these inclusions diminishes after the HBr treatment, and their effect on the mass budget of Pb released during the subsequent HNO_3 step can hardly be noticed after step [4]. In the HF steps [5a] and [5b] increasingly uranium Pb appears while thorogenic Pb isotope ratios remain constant. This can be explained by an increased influence on the mass budgets in the leach solutions by Pb from micro-inclusions of zircon as dissolution rate (HF-attack) progresses from step to step. In step [5c] finally more common Pb appears and the mass budget of Pb in this solution was probably dominated by garnet. The "zircon" trend in figure 2b is therefore defined by differentially released common and slightly radiogenic Pb from garnet, and highly radiogenic Pb from zircon inclusions.

All PbSL data together yield an apparent isochron date of 2602 ± 40 Ma (MSWD = 0.60, Fig. 2a). An isochron age of 2587 ± 45 Ma (MSWD = 0.15) results when the two highly radiogenic steps [2] and [3] are excluded. This represents a monazite-free date. The tie line between step [1] and steps [2] and [3] defines an age of 2656 ± 71 Ma (MSWD = 0.06) and is consequently interpreted as a minimum age for monazite inclusions. Although the line defined by steps [1] and [5 a-c]

incorporate data from two phases (garnet and zircon) it is not a two-component (mixing line as more or less radiogenic Pb from both phases is involved. If either the zircon was significantly older than 2.6 Ga or the garnet significantly younger than 2.6 Ga, no isochron would have resulted. We therefore conclude that both phases formed during the 2.6 Ga event. In spite of the slight differ-

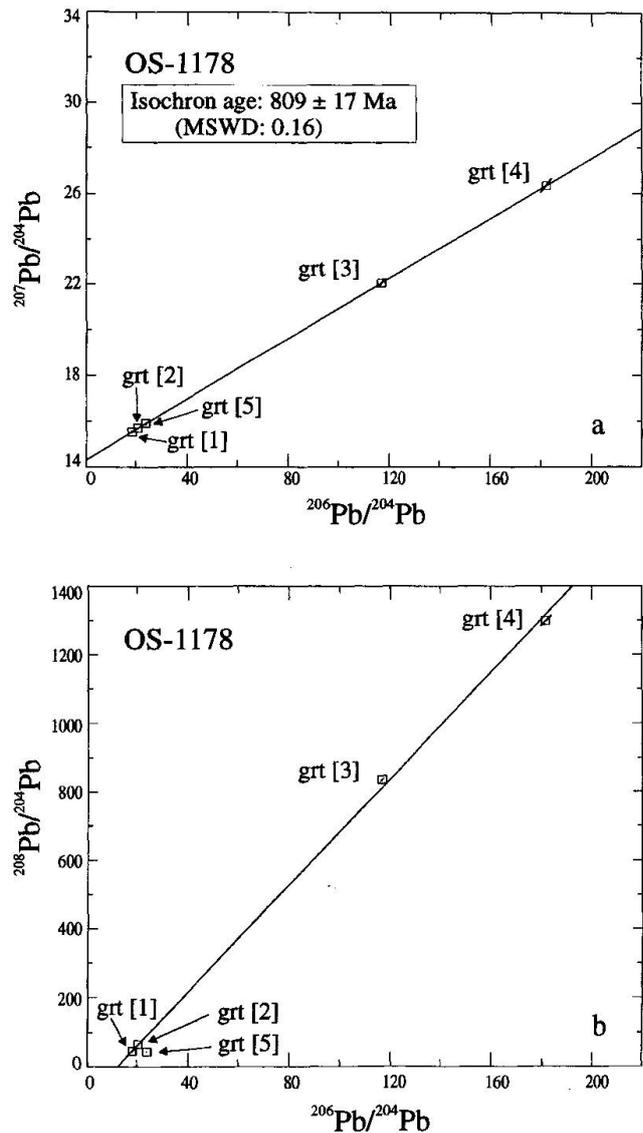


Fig. 1 (a) Uranogenic Pb isotope diagram with PbSL data of garnet from sample OS-1178. Step codes in squared brackets correspond to slightly modified recipes in FREI and KAMBER (1995). The isochron of 809 ± 17 Ma, together with the linear data arrangement in figure 1b, indicates that a single phase "garnet" was leached, i.e. that possible submicroscopic inclusions play a minor role in the Pb budgets of the leach solutions. (b) Thorogenic Pb isotope diagram with the same data as in figure 1a. The linear array defined by the PbSL data points indicates a single phase "garnet" with only minor contamination by possible zircon inclusions as depicted by the slight offset of step [5] (see text).

ence with the monazite age it is not excluded that garnet and zircon crystallized in equilibrium with monazite also, which would explain their extremely low Th/U ratio. On the basis of the PbSL data presented herein, and in contrast with PbSL data from the Proterozoic Triangle Shear Zone,

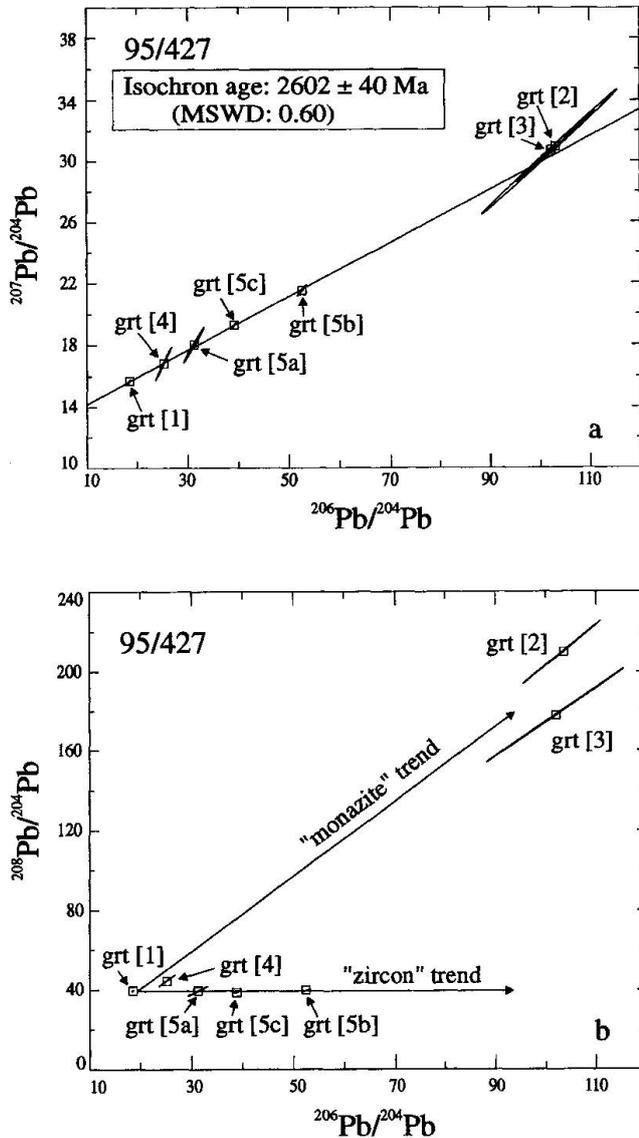


Fig. 2 (a) PbSL data of garnet from sample 95/427 plotted in the uraniumogenic Pb isotope diagram. Step [2] and [3] are dominated by Pb from monazite inclusions (see Fig. 2b; "monazite" trend). The isochron age of 2602 ± 44 Ma including all the PbSL however indicates that isotope equilibrium between the host garnet and the inclusions was reached at the time of formation of the former. (b) Same data set as in figure 2a, plotted in the thorogenic Pb isotope diagram. Steps [2] and [3] are characterized by highly thorogenic Pb compatible with a derivation from monazite ("monazite" trend). The "zircon" trend (characterized by constant $^{208}\text{Pb}/^{204}\text{Pb}$) is interpreted as a two component mixing line between Pb from garnet itself and from possible micro-inclusions of zircon (see text).

we can exclude garnet 95/427 to have grown during a 2.0 Ga granulite-facies metamorphic event in the Palala Shear Zone, although similarity with conditions met in the Triangle Shear Zone (KAMBER et al., 1995, and references therein) are proposed from field observations. An alternative case in which the PbSL release pattern of a garnet sample is extensively affected by monazite inclusions has been reported by FREI and KAMBER (1995). In this investigation the data points do not define an isochron (unlike in all the examples presented herein) but rather a curve similar to a hyperbola in the uraniumogenic diagram. Thus the step leaching approach in this case was capable of showing an additional complexity of the U-Th-Pb system in this mineral, in that it clearly revealed the presence of isotopically unequilibrated, older monazite inclusions.

SAMPLE LF-1

PbSL data from sample LF-1 are plotted in figure 3a (uranogenic diagram) and 3b (thorogenic diagram), with data listed in table 1. The first three steps yielded increasingly uraniumogenic Pb compositions, followed by step [4] during which an even more primitive Pb than the one from step [1] was leached. The uraniumogenic spectrum is dominated by two very radiogenic values which are characterized by $^{206}\text{Pb}/^{204}\text{Pb}$ of 307 and 261. Both compositions were measured in the residual steps [5a, 5b] in which HF attacks were applied. In the thorogenic diagram (Fig. 3b) a quasi-linear array is spanned by PbSL data of steps [3] to [5b], whereas the first two steps diverge from this line by their slightly elevated thorogenic compositions with $^{208}\text{Pb}/^{204}\text{Pb}$ ratios around 47.5. PbSL data define an isochron of 1716 ± 27 Ma (MSWD = 1.43).

Thus a twofold data distribution is again observed in the thorogenic diagram. It is characterized by a strong offset of the two first leach steps from a well defined linear arrangement of data from the successive leaching steps. The latter are dominated by highly uraniumogenic Pb recovered from the two residual HF-attacks. This spectrum clearly reveals the presence of three phases. The first two steps are characterized by slightly elevated $^{208}\text{Pb}/^{204}\text{Pb}$ ratios compared to Pb released from garnet (intermediate steps [3] and [4]). From our observation that minute relic amphibole grains adhere to garnet surfaces, it is likely that this mineral is a contaminant. This is supported by the similarity of the release pattern with that from amphiboles (FREI and KAMBER, 1995), which indicates an easily recoverable, slightly thorogenic Pb from the lattice at the beginning of a PbSL exper-

iment. The process by which increased data spread is obtained during stepwise leaching can, for amphibole, be interpreted as described in FREI et al. (1997), i.e. by a combination of a destruction of the lattice hydrolysis of the surface with concomitant removal of Ca and substituting common Pb into the leach solution. The quasi-linear arrangement of the successive leaching steps (Fig. 3b) again is interpreted to derive from a two-component mixing between Pb originating from gar-

net itself and zircon inclusions, respectively. The last two leaching steps yield the most radiogenic Pb. In garnet, the last steps generally yield a trend towards more common Pb as in the case of sample OS-1178; therefore the radiogenic Pb released in these final HF steps points to zircon inclusions as its most likely source. The Pb measured from those final dissolution steps dominates the spread in the uranium diagram (Fig. 3a) and therefore also the precision of the age. All PbSL data define an isochron of 1716 ± 27 Ma (MSWD = 1.43) although the age from the data points ascribed to garnet is imprecise, it is fully consistent with the field interpretation, i.e. that these garnets and the zircon inclusions grew during the emplacement of the Harney Peak granite at ~ 1715 Ma within its contact aureole with the country rock sediments. Further, the data provide indirect evidence for a Pb isotope equilibrium between surface related amphibole contaminants, micro-inclusions of zircon and the host garnet.

A number of general observations from the three different PbSL spectra of garnet can be made: First, the initial leaching step is consistently characterized by a non-radiogenic Pb isotope composition. This Pb isotope signature could be of importance for alternative implications, as it may very closely approximate the initially built-in Pb composition and therefore can be used for comparative genetic tracing. The above observation is consistent with the predictions and interpretations by FREI et al. (1997), who support the contention by experiments, that the first leaching step is likely to be dominated by surface-hydrolysis-dominated Pb-release from the silicate mineral structure. Second, prolonged strong HBr steps have shown to be able to recover quantitatively Pb from monazite inclusions in garnet which therefore enables the subsequent leaching of garnet-hosted Pb. PbSL may be applied prior to bulk U-Pb garnet dating as it offers the possibility to delineate whether or not inclusions were in isotope equilibrium with their host at the time the latter crystallized. This may help to prevent erroneous and geologically meaningless bulk mineral age dating. Third, the presence of zircon rather than monazite can be traced via the isotope signature of the residual HF attacks. Zircon has shown to contribute Pb only during longer lasting HF steps, as this mineral is highly resistant towards the other acids. Care has to be taken as Pb from zircons may dominate the final dissolution steps and therefore may affect the apparent age of the host mineral. The combined investigation of uranium and thorogenic Pb release during the various leaching steps however allows to con-

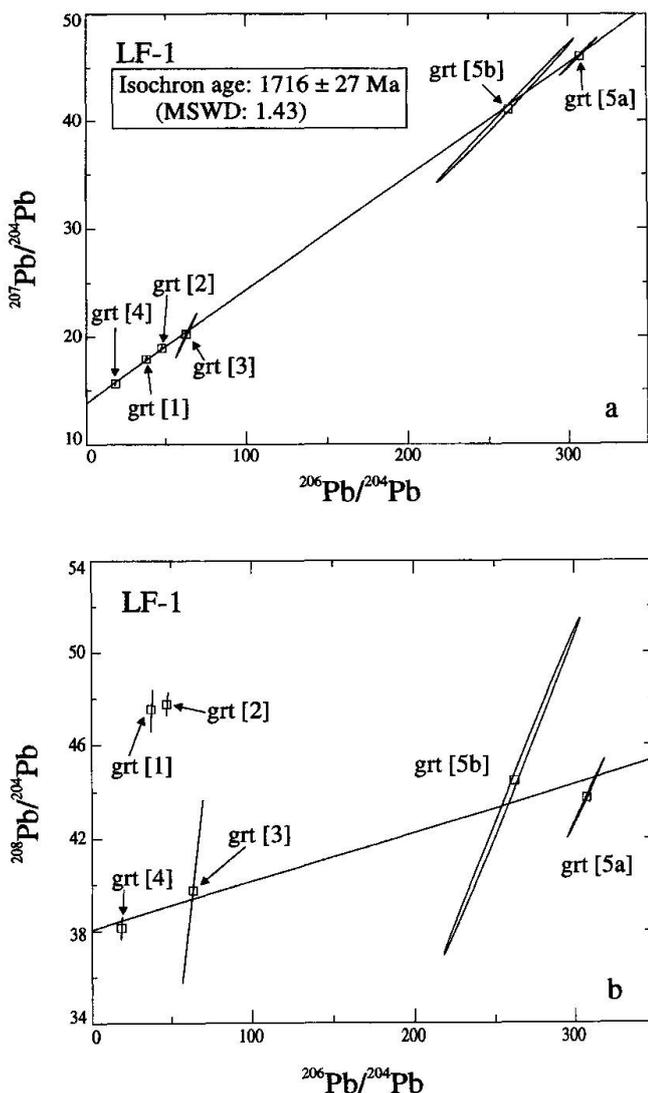


Fig. 3 (a) Leach spectrum of sample LF-1 in the uranium Pb isotope diagram. Despite indications for Pb to derive from at least three different phases (see Fig. 3b), isotope equilibrium is manifested by the isochron in this diagram (1716 ± 27 Ma). (b) Thorogenic Pb isotope diagram of the PbSL data from sample LF-1. The data spectrum is characterized by an offset of the two first leach steps from a quasi-linear array spanned by PbSL data of steps [3] to [5b]. The former is interpreted to result from grain surface hornblende contaminants (see text), whereas the latter is seen as a mixing trend between zircon inclusions and host garnet.

strain whether or not the microscopically small zircon inclusions were in isotope equilibrium with each other and with garnet at the time of its formation. Finally, PbSL of an essentially inclusion-free garnet behaves concomitantly to that performed on titanite (FREI et al., 1997), in that first increasingly and later on again less radiogenic Pb isotope compositions are recovered from the sample material. This behavior is consistent with the proposed combined surface hydrolysis-selective cation absorption mechanism (FREI et al., 1997) responsible for a spread in Pb isotope data during PbSL. Our data on sample OS-1178 support the results by FREI et al. (1997) and imply that PbSL dating can be applied to inclusion-free garnet, i.e. that heterochemical inclusions are not a necessary prerequisite for obtaining an enhanced $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ data spread.

Conclusions

This study has revealed the potential of PbSL to dating compositionally different metamorphic garnets and supports previous positive attempts to dating this rock-forming mineral. The combination of stepwise leaching spectra in the uraniumogenic vs thorogenic Pb isotope array allows to delineate clearly the presence of optically unrecognized solid inclusions (monazite and zircon), and by comparison with the data arrangement in the isochron diagram, provide information on whether or not inclusions were in isotope equilibrium with each other and with their host at the time of its crystallization. HBr has proven effective in selectively and quantitatively removing Pb from monazite inclusions and therefore enables subsequent monazite-free PbSL dating of garnet. The presence of zircons may be detected from the Pb isotope compositions of HF residual attacks. PbSL as a tool for dating rock-forming silicates potentially increases the credibility of ages obtained and therefore helps to prevent erroneous interpretation when put in relation with independent geological constraints.

Acknowledgements

This study stems from a number of interdisciplinary projects of members of the Gruppe für Isotopengeologie and summarizes experiences gained from the application of PbSL to rock-forming minerals. We would like to express our thanks to the many persons in our lab who contributed to discussions related to this issue. Furthermore we are thankful to Felix Würsten whose sample OS-1178 from his Dissertation-project was used for this study. Sample LF-1 was provided by Peter Dahl and is

part of a sample batch used in a joint garnet dating project between the former and RF in the Black Hills (South Dakota). Helpful review was provided by Klaus Mezger. We are furthermore indebted to the Swiss National Foundation 20-40442.94 to JDK.

References

- BARTON JR., J.M., HOLZER, L., KAMBER, B.S., DOIG, R., KRAMERS, J.D. and NYFELER, D. (1994): Discrete metamorphic events in the Limpopo belt, southern Africa: implications for the application of P-T paths in complex metamorphic terrains. *Geology* 22, 1035–1038.
- BLENKINSOP, T.G. and FREI, R. (in press): Archean and Proterozoic mineralization and tectonics at Rencome mine (Northern Marginal Zone, Limpopo Belt, Zimbabwe). *Econ. Geol.*
- BUICK, I.S., FREI, R. and CARTWRIGHT, I. (subm.): The timing of high-temperature retrogression in the Reynolds Range, central Australia; constraints from single mineral Pb–Pb dating.
- BURTON, K.W. and O'NIONS, R.K. (1991): High-resolution garnet chronometry and the rates of metamorphic processes. *Earth and Planet. Sc. Lett.* 107, 649–671.
- DEWOLF, C.P. and MEZGER, K. (1994): Lead isotope analyses of leached feldspars: Constraints on the early crustal history of the Grenville Orogen. *Geochim. et Cosmochim. Acta* 58, 5537–5550.
- DEWOLF, C.P., ZEISSLER, C.J., HALLIDAY, A.N., MEZGER, K. and ESSENE, E.J. (1996): The role of inclusions in U–Pb and Sm–Nd garnet geochronology: Stepwise dissolution experiments and trace uranium mapping by fission track analysis. *Geochim. et Cosmochim. Acta* 60, 121–123.
- FREI, R. (1996): The extent of inter-mineral isotope equilibrium: a systematic bulk U–Pb and step-leach Pb isotope study of individual phases from the Tertiary granite of Jerissos (Northern Greece). *Eur. J. of Mineral.* 8, 1175–1189.
- FREI, R. (1995): A new Pb-dating technique for gold deposits: Examples from Zimbabwe: Extended abstract, Centennial Geocongress, Geological Society of South Africa, Johannesburg (South Africa), 3–7 April, 64–67.
- FREI, R., BIINO, G.G. and PROSPERT, C. (1995): Dating a Variscan pressure-temperature loop with staurolite. *Geology* 23, 1095–1098.
- FREI, R. and KAMBER, B.S. (1995) Single mineral Pb–Pb dating. *Earth and Planet. Sci. Lett.* 129, 261–268.
- FREI, R. and PETTKE, T. (1996): Mono-sample Pb–Pb dating of pyrrhotite and tourmaline: Proterozoic vs Archean gold mineralization in Zimbabwe. *Geology* 24, 823–826.
- FREI, R., VILLA, I.M., NÄGLER, Th.F., KRAMERS, J.D., PRZYBYLOWICZ, W.J., PROZESKY, V.M., HOFMANN, B.A. and KAMBER, B.S. (1997): Single mineral dating by the Pb–Pb step-leaching method: assessing the mechanism. *Geochim. et Cosmochim. Acta.* 61, 393–414.
- HOLM, D.K., DAHL, P.S. and LUX, D.R. (subm.): $^{40}\text{Ar}/^{39}\text{Ar}$ evidence for Middle Proterozoic cooling of the Southern Black Hills, South Dakota, and implications for Early Proterozoic tectonothermal evolution. *Tectonics.*
- HOLZER, L., KAMBER, B.S., KRAMERS, J.D. and FREI, R. (in press): The tectono-metamorphic event at 2 Ga

- in the Limpopo Belt and the resetting behaviour of chronometers at high temperature. *Special Publ. Geol. Survey Namibia*.
- KAMBER, B.S., BLENKINSOP, T.G., VILLA, I.M. and DAHL, P.S. (1995): Proterozoic transpressive deformation in the Northern Marginal Zone, Limpopo Belt, Zimbabwe. *J. Geol.* 103, 493–508.
- KROGSTAD, E.J. and WALKER, R.W. (1994): High closure temperatures of the U–Pb system in large apatites from the Tin Mountain pegmatite, Black Hills, South Dakota, USA. *Goechim. et Cosmochim. Acta* 58, 3845–3853.
- LANZIOTTI, A. and HANSON, G.N. (1995): U–Pb dating of major and accessory minerals formed during metamorphism and deformation of metapelites. *Goechim. et Cosmochim. Acta* 59, 2513–2526.
- LUDWIG, K.R. (1988): A computer program to convert raw U–Th–Pb isotope ratios to blank-corrected isotope ratios and concentrations with associated error-correlations. *USGS Open-file Report OF-88-0557*.
- MEZGER, K., HANSON, G.N. and BOHLEN, S.R. (1989): U–Pb systematics of garnet: dating the growth of garnet in the Late archaean Pikwitonei granulite domain at cauchon and Natawahunan lakes, Manitoba, Canada. *Contr. Mineral. and Petrol.* 101, 136–148.
- MEZGER, K., RAWNSLEY, C.M., BOHLEN, S.R. and HANSON, G.N. (1991): U–Pb garnet, sphene, monazite, and rutile ages: implications for the duration of high-grade metamorphism and cooling histories, Adirondack Mts., New York. *J. Geol.* 99, 415–428.
- NÄGLER, Th.F., HOLZER, L. and FREI, R. (1996): What dominates the Nd and Pb characteristics of garnet? *Journal of Conference Abstracts, Sixth V.M. Goldschmidt conference, 31 March – 4 April, Heidelberg, Germany, 1, 424.*
- NÄGLER, Th.F., HOLZER, L. and FREI, R. (1995b): Nd and Pb in monazite inclusions within polymetamorphic garnets: hell or heaven? Abstract, EOS, Transactions, American Geophysical Union, Fall Meeting, 11–15 December 1995, 76/46, F707.
- REDDEN, J.A., PETERMAN, Z.E., ZARTMAN, R.E. and DEWITT, E. (1990): U–Th–Pb geochronology preliminary interpretation of Precambrian tectonic events in the Black Hills, South Dakota. In: LEWRY, J.F. and STAUFFER, M.R., (eds): *Canada Special Paper 37, 229–251.*
- SCHÖNBERG, R. (1996): The Precambrian Crystalline Basement of the Sadh area (Dhofar area, Sultanate of Oman). Unpublished diploma thesis, University of Berne, Switzerland.
- VANCE, D., BELSHAW, N.S. and O'NIONS, R.K. (1991): U–Pb chronometry of metamorphic garnets: a comparison of TIMS analysis of garnet and high resolution SIMS analysis of U-rich inclusions. *EOS* 72, 560.
- WÜRSTEN, F. (1994): The Precambrian Crystalline Basement of Salalah (Dhofar area, Sultanate of Oman). Ph. D. Thesis, University of Berne, Switzerland.
- VAN REENEN, D.D., ROERING, C., ASHWAL, L.D. and DE WIT, M.J. (1992): Regional geological setting of the Limpopo Belt. *Precambrian Research* 55, 1–5.

Manuscript received October 24, 1996; revised manuscript accepted January 20, 1997.