

Sphene (titanite): phase relations and role as a geochronometer

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Abstract

Useful U–Pb isotopic data may be obtained from sphene (or titanite, CaTiSiO₅) because: (1) it is a widespread accessory mineral, (2) it can incorporate uranium in its structure, and (3) it has a high closure temperature. In igneous rocks, sphene is most abundant in relatively oxidized rocks, such as metaluminous rocks of intermediate composition. These rocks have the high Ca/Al ratios wherein sphene is stabilized relative to ilmenite + quartz or ilmenite + anorthite. In metamorphic rocks, sphene is stable to the highest temperatures in mafic and calc-silicate rocks. It is found mostly in greenschist, blueschist, and amphibolite facies, although in calcic rocks its stability may extend into granulite facies. Recent studies show that the closure temperature for sphene lies at the upper limit of amphibolite facies. Because sphene reacts readily during metamorphism, U–Pb sphene ages are likely to yield the age of metamorphic crystallization, rather than resetting by simple diffusion. For this reason, metamorphic sphene may yield complex U–Pb systematics that contain information on the whole metamorphic history of the rock.

Sphene from igneous rocks and orthogneisses has initial U contents ranging from 10 to over 100 ppm and ratios of initial U to common Pb ranging from 10 to 1000, ratios that may potentially yield high precision U–Pb ages. Sphene in marbles, calc-silicates, and metagraywackes has a similar range in composition to that from igneous rocks, but sphene from metabasites may have initial U contents of less than 1 ppm and ratios of initial U to common Pb lower than 1, making them unsuitable for geochronology. These low-U sphenes are most commonly found in weakly metamorphosed metabasites. Strategies to extract age information from sphene with moderate initial U/common Pb ratios include estimation of common Pb isotopic composition of sphene from coexisting low-U phases, use of U–Pb and Pb–Pb isochron plots, and step-wise leaching methods to improve ²⁰⁶Pb/²⁰⁴Pb spread. By correlating sphene compositions to metamorphic or hydrothermal reactions, age determinations on sphene can be used to directly date metamorphism, deformation, and hydrothermal alteration. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Sphene (CaTiSiO₅) is a widespread accessory mineral that, because small amounts of uranium may be in its structure, is an important mineral for U–Pb

dating. Because sphene has a high closure temperature (up to 700°C), it, like zircon, can provide important information on the age of high-temperature events. Sphene, however, behaves very differently in a high temperature environment than does zircon. Zircon is the only Zr-rich mineral in most rocks and can participate in reactions only if it interacts with Zr-bearing fluids or with Zr that has been dissolved

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in trace amounts in other phases in the rock. Consequently, U–Pb systematics in zircon retain information on original igneous crystallization events, although minor zircon overgrowths in high-grade rocks are not uncommon. Because most rocks contain numerous phases that may contain Ti and Ca, sphene, in contrast to zircon, is quite reactive in high temperature environments (Scott and St. Onge, 1995). Consequently, U–Pb systematics are much more likely to be affected by multiple stages of growth in sphene than in zircon.

Sphene can occur both as a primary igneous mineral, as a mineral formed in igneous rocks during cooling and as a metamorphic mineral in many rock types. To utilize it most efficiently as a way to date igneous processes, metamorphism, or deformation, we must understand the factors that control its occurrence and composition in igneous and metamorphic rocks. In this paper, we discuss the crystal chemistry of sphene and how it accommodates U and Pb, the factors that control sphene stability in nature and how the composition of sphene reflects the temperature and pressure of formation. Utilizing these data, we present strategies whereby one can most efficiently use sphene as a chronometer.

2. Crystal chemistry of sphene

The structure of sphene consists of chains of Ti-octahedra that are bonded together by isolated Si-tetrahedra (see Fig. 1). The structure contains four

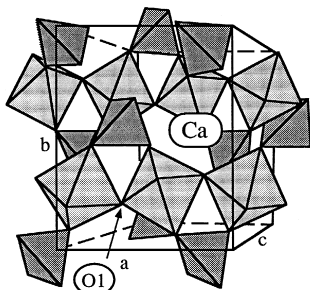


Fig. 1. Three-dimensional sketch of the structure of sphene showing the tetrahedral sites (dark stippling), the octahedral Ti-site (light stippling) and the Ca and O1 sites (modified after Taylor and Brown, 1976).

sites in which cations may substitute. In addition to the octahedral Ti site and the tetrahedral Si site, there is the large sevenfold Ca site and the underbonded O1 Site (Ribbe, 1980). The tetrahedral site is usually filled with silicon (Ribbe, 1980; Franz and Spear, 1985). Recent work by Oberti et al. (1991) has shown that there is no consequential substitution of Ti^{4+} for Si^{4+} at the tetrahedral site. Additionally, the volume of the octahedral site decreases linearly with increasing X_{Al} , and the volume of the Ca site is linearly dependent on the size of the octahedral site. Hence, substitution of Al at the octahedral site causes contraction of the VII-coordinated site, but the tetrahedral site is unaffected (Oberti et al., 1991). Chemical substitutions in nature occur only in the other three sites.

2.1. Ca-site

The sevenfold Ca site takes all the large ions, including REEs, U, Th, Mn and Pb (Higgins and Ribbe, 1976). In sphene from pegmatite, REEs may total over 4 wt.% (Deer et al., 1982), although in sphene from most rocks REEs are below microprobe detection (i.e. < ca. 0.02%).

2.2. Ti-site

The Ti site contains Al and Fe (usually the Fe is considered to be Fe^{3+} , although Fe^{2+} may be present also). Other high valance ions such as Zr, Ta and Nb also may be present. Sphene has been reported with up to 14% Al_2O_3 (Franz and Spear, 1985), and up to 3.0% Fe_2O_3 (Deer et al., 1982); and with more than 20% Ta_2O_5 and up to 5% Nb_2O_5 (Cérny' et al., 1995), although in most rocks the minor element content of sphene is low.

2.3. Underbonded O1 site

The oxygen that connects the Ti octahedra together is known as O1 and it is slightly underbonded compared to other oxygens in the structure. This underbonded oxygen may be replaced by ions such as OH or F (Ribbe, 1980).

3. Controls of sphene stability

3.1. Sphene stability in igneous rocks

3.1.1. Effects of bulk composition

Because of its calcic composition sphene is most commonly found in rocks rich in calcium. Several authors have noted that the Ca/Al ratio of a rock is important in determining the presence of sphene (Thieblemont et al., 1988; Force, 1991). High Ca activities will tend to drive reactions (1) and (2) (Table 1) to the right, stabilizing sphene instead of quartz + ilmenite or quartz + ilmenite + K-feldspar. Conversely, high Al activity in the melt will drive reaction (3) to the right, causing anorthite + ilmenite to form instead of sphene. This explains why sphene is most commonly found in metaluminous, I-type granitoids of intermediate SiO₂ contents (such as

diorites and granodiorites). Sphene may be absent in the most siliceous granites, because CaO decreases with increasing SiO₂, precluding the formation of sphene. Similarly, sphene is rare in peralkaline granitoids and in peraluminous granites because rocks with these chemical characteristics will have low Ca/Al ratios.

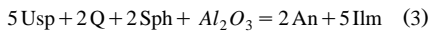
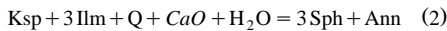
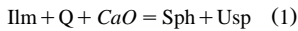
3.1.2. Effects of intensive parameters (*P*, *T*, and fluid composition)

In mafic rocks, which have the high Ca/Al ratio necessary for sphene crystallization, sphene stability is controlled more by the conditions of crystallization than by bulk composition. In rocks containing anhydrous Fe-Mg silicates, sphene stability is independent of oxygen fugacity at temperatures below the reaction of sphene + fayalite = hedenbergite + ilmenite (reaction 4 displaced to account for solid solution) (Wones, 1989). Experimental work of Xirouchakis and Lindsley (1998) shows that in the pure system Ca-Fe-Ti-Si-O this reaction lies around 600°C at 3 kbar. Above this temperature, the stability of sphene is strongly controlled by oxygen fugacity, where the limiting reaction is sphene + ulvöspinel + quartz = hedenbergite + ilmenite (where ulvöspinel is a component in magnetite and hedenbergite is a component in augite, Table 1, reaction 5) (Xirouchakis and Lindsley, 1998). Because the composition of Ti-magnetite and ilmenite are dependent on oxygen fugacity, the location of reaction (5) is dependent on *T*, *f*_{O₂}, and the Fe-Mg content of the silicates ($\mu_{\text{FeMg}_{-1}}$) (Fig. 2). For iron-rich rocks, sphene stability may extend down to conditions of the FMQ buffer, but for magnesian rocks it may be restricted to oxygen fugacities of 1 or more units above FMQ. This restriction of sphene to relatively oxidizing conditions applies only to anhydrous assemblages. In hydrous environments, sphene is stabilized by either reaction (7) hedenbergite + ilmenite + quartz + H₂O = sphene + Fe-actinolite, or in quartz-absent rocks reaction (8) hedenbergite + ilmenite + H₂O = Fe-actinolite + sphene + ulvöspinel (where ferroactinolite is a component in hornblende and ulvöspinel is the Ti-component in magnetite) (Fig. 3). Although reactions (5) through (8) in Table 1 are independent of oxygen, they appear in Fig. 3 as being oxygen-dependent because

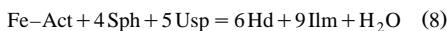
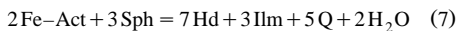
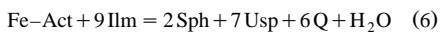
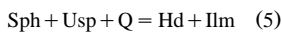
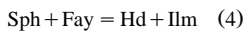
Table 1

Reactions controlling sphene stability in igneous rocks

Reactions demonstrating compositional control for sphene



Reactions controlling sphene in mafic rocks



An = anorthite, Ann = annite, Fay = fayalite, Fe-Act = ferroactinolite, Hd = hedenbergite, Ilm = ilmenite, Ksp = K-feldspar, Q = quartz, Sph = sphene, Usp = ulvöspinel, *italics* = components in melt.

the abundance of the ilmenite and ulvöspinel components in the rhombohedral and cubic oxides are oxygen-dependent.

The constraints on sphene stability noted above correlate well with the observed occurrence of sphene in igneous rocks. In most igneous rocks, the stable Ti-phases are titanomagnetite and ilmenite (Frost and Lindsley, 1991), rather than sphene, indicating that they crystallized at oxygen fugacities too low for the stability of sphene. Sphene is found in relatively oxidized rocks (Wones, 1989) (Fig. 2) and is far more likely to be found in the presence of hornblende than in anhydrous rocks.

Although sphene is common in plutonic calc-alkalic rocks, it is rare in eruptive rocks of the same composition (compare Frost and Lindsley, 1991). This suggests that sphene found in many calc-alkalic plutonic rocks formed late in the crystallization history of the magma. There are two processes by which sphene could form during cooling of plutonic rocks. It could form in association with the hydration of pyroxenes to hornblende (i.e. reaction 7 or 8). Depending on the activity of water in the melt, this hydration could occur either in the magmatic state or during deuteric alteration. Sphene could also form by oxidation during postmagmatic reequilibration if a typical calc-alkalic rock were to follow an ilmenite-dominated cooling trend. Such trends may be strongly oxidizing (Frost, 1991) and could drive the rock to higher relative oxygen fugacity, causing it to cross into the stability field of sphene.

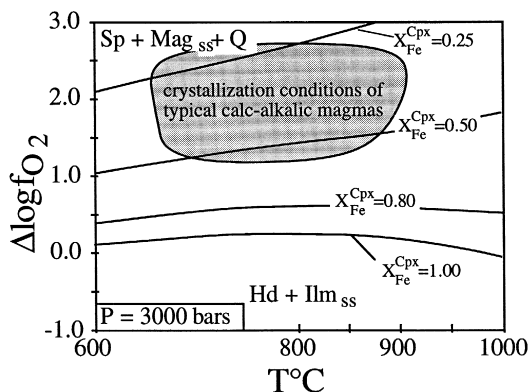


Fig. 2. $\log f_{O_2}$ - T diagram for the stability of sphene in anhydrous rocks contoured for the composition of clinopyroxene. $\log f_{O_2}$ is the deviation from the FMQ buffer. Calculated from the data of Xirouchakis and Lindsley (1998).

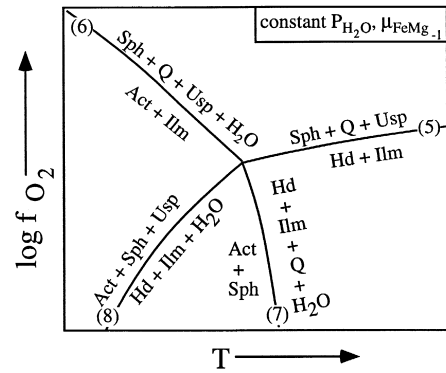


Fig. 3. Schematic $\log f_{O_2}$ - T diagram showing the effect of hydration reactions on the stability of sphene in mafic rocks.

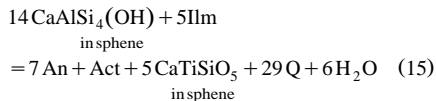
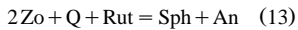
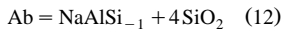
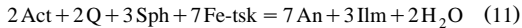
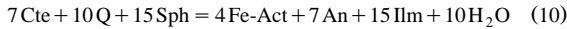
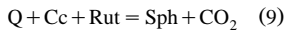
3.2. Sphene in metamorphic rocks

As with igneous rocks, the occurrence of sphene in metamorphic rocks is strongly controlled by bulk composition. For example, sphene survives to higher temperatures in calcic rocks (such as impure marbles) than in metapelitic rocks. Among the rock types that commonly contain sphene are the following.

3.2.1. Calc-silicate rocks and marbles

Sphene is widespread in calcium-rich metamorphic rocks that have formed from: (1) marly sediments or impure limestones that originally contained Ti-bearing detritus, or (2) metasomatic reaction zones at boundaries between carbonates and Ti-bearing rocks (such as metapelitic and mafic rocks) (Cliff et al., 1993; Romer and Nisica, 1995). A major reaction limiting sphene stability in these rocks is reaction (9) (Table 2) (Hunt and Kerrick, 1977), whereby rutile + calcite + quartz react to sphene. Fig. 4 shows that this reaction restricts sphene to low pressures or to fluids having relatively low X_{CO_2} . Sphene does occur in eclogite-grade marbles (Franz and Spear, 1985; Castelli, 1991; Boundy et al., 1997), where, as noted below, it may be stabilized by high Al and F contents (Carswell et al., 1996). In some areas, sphene in calc-silicate rocks appears to break down to ilmenite in amphibolite facies (Carmichael, 1970); whereas, in other areas it is stable well into granulite facies (Motoyoshi et al., 1991; Dasgupta, 1993; Mezger et al., 1993; Corfu et al., 1994; Zalduegui et al., 1996).

Table 2
Equilibria controlling sphene stability during metamorphism



Ab = albite, Cc = calcite, Cte = chlorite, Fe-tsk = Fe-tschermakite ($Ca_2Fe_4AlSi_7AlO_{22}(OH)_2$), Lw = lawsonite, Rut = rutile, Zo = zoisite, other abbreviations as in Table 1.

3.2.2. Metabasites

As suggested by reaction (7), sphene occurs commonly in metabasites over a wide range of metamorphic conditions. Fig. 5 shows a poorly constrained diagram for the stability of sphene in metabasites,

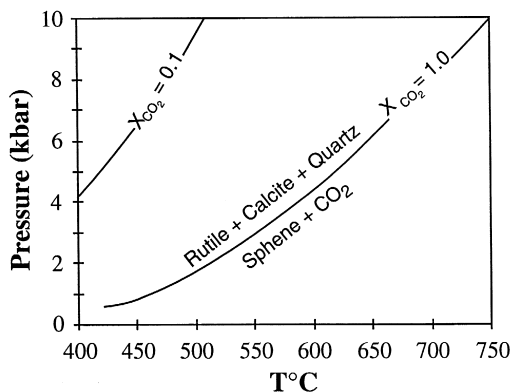


Fig. 4. P - T diagram showing the stability of sphene in calcite-bearing rocks. Calculated from the data of Berman (1988) and Xirouchakis and Lindsley (1998).

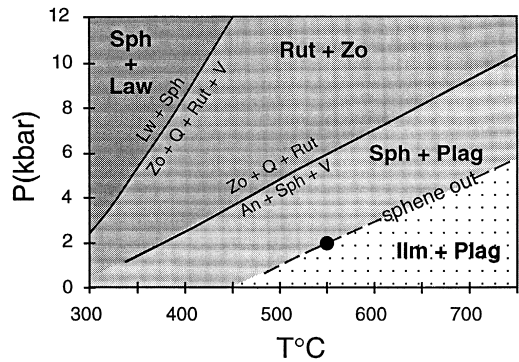


Fig. 5. P - T diagram showing the approximate stability fields of ilmenite, sphene, and rutile in metabasites. See text for discussion.

based upon natural assemblages, a few experimental points, and thermodynamic calculations. Sphene is the main Ti-bearing phase in weakly metamorphosed mafic rocks (Force, 1976; Zen, 1974; Beiersdorfer, 1993); ilmenite appears in upper greenschist (Cassidy and Groves, 1988) and lower amphibolite facies (Peacock and Norris, 1989). The reactions that remove sphene from metabasites with increasing T probably involve extraction of CaO from sphene to form plagioclase. At low temperatures, reaction (10) may apply, while at higher T , where chlorite would not be stable in metabasites, reaction (11) could be the controlling reaction. In quartz-undersaturated rocks, reactions (10) and (11) may progress in combination with reaction (12), which governs the breakdown of albite to edenite component in hornblende.

The high-temperature limit for sphene in Fig. 5 has been taken from experiments by Liou et al. (1974), Spear (1981) and Hellman and Green (1979). Liou et al. (1974) determined one reversed point for a reaction similar to reaction (10) at 2 kbar and 550°C (black dot in Fig. 5) and showed the sphene-out reaction to have a steep slope (dP/dT). Spear (1981) in contrast shows it to have a much gentler slope. In constructing Fig. 5, we have chosen Spear's slope for the curve and have moved it slightly to lower temperatures so that it would pass through the 2-kbar reversal of Liou et al. We justify this for two reasons: (1) in their text, Liou et al. (1974) specify that the only point where they can be sure their reaction is a reversal is at 2 kbar. The presence of minor phases is not listed in their tables so it is impossible to determine whether sphene also disap-

pears with chlorite in the high temperature points. (2) Hellman and Green (1979) report sphene stable in mafic rocks to 1020°C and 16 kbar. This is more in agreement with the slope suggested by Spear than that given by Liou.

The pressure-dependence of the sphene-out reaction (reactions 10 and 11) is seen in the assemblages reported from the literature. For example, in the low-pressure rocks from the Karmutsen volcanic rocks sphene disappears at about the grade where hornblende appears (Terabayashi, 1993). In higher-pressure amphibolites sphene disappears in the middle of amphibolite facies (Ghent and DeVries, 1972; Begin, 1990, 1992). In high pressure granulites from Sri Lanka ($P = \text{ca. } 8 \text{ kbar}$) sphene persists to granulite facies (Schumacher et al., 1990) and it is also found in mafic granulites from the Yilgarn Craton (Nemchin et al., 1994). The only natural occurrence of sphene breakdown that does not fit this pattern is its reported disappearance in mafic rocks from the Sanbagawa during the transition from blueschist to amphibolite facies (Otsuki and Banno, 1990). The comparatively low temperature at which ilmenite appears in these rocks can be explained by the fact that it is rich in Fe_2O_3 (it has a comparatively low FeTiO_3 activity), stabilizing it to lower temperatures.

The high-pressure limit for sphene in plagioclase-bearing rocks is the reaction of sphene + plagioclase to epidote-rutile-quartz (reaction 13). The position of this boundary on (Fig. 5) has been calculated from the database of Berman (1988) using pure phases. Plagioclase and zoisite in metabasites commonly contain moderate amounts of $\text{NaAlSi}_3\text{O}_8$ and $\text{Ca}_2\text{Al}_2\text{Fe}^{3+}(\text{Si}_3\text{O}_{12})(\text{OH})$, respectively. These substitutions will have competing effects on the P - T position of reaction (13), but it is evident from natural assemblages that the location of this reaction lies at somewhat higher pressures than indicated in Fig. 5. For example, rutile and epidote occur commonly in eclogites (Force, 1991) and high temperature blueschists but low-temperature blueschists and eclogites may contain sphene (commonly in association with rutile, Honegger et al., 1989). Furthermore, the formation of sphene rims on rutile is a common decompression texture in high- P rocks (Ghent et al., 1993; Klemd et al., 1994), but the assemblage epidote-rutile is recorded only in very high pressure ($T = 500^\circ\text{C}$, $P > 10 \text{ kbar}$) amphibolites (Rötzler et

al., 1999). This indicates that in natural rocks reaction (13) lies somewhere in the stability of blueschist facies (i.e. $P > 6 \text{ kbar}$ at 400°C (Evans, 1990), but that it may extend into lower amphibolite facies at pressures above 10 kbar.

The stability of rutile in mafic rocks is limited at high pressures and low temperatures by the reaction $\text{rutile} + \text{zoisite} + \text{quartz} = \text{sphene} + \text{lawsonite}$ (reaction 14). This is consistent with the fact that high pressure rocks with lawsonite contain sphene instead of rutile (El-Shazly, 1994).

3.2.3. Other metasedimentary rocks

Sphene is found in pelitic rocks only in low grades (Enami, 1983; Baltatzis and Katagas, 1984; Force, 1991), although in some weakly metamorphosed pelitic rocks carbonate + rutile may be present instead (Ferry, 1984). Itaya and Banno (1980) report that sphene disappears from pelitic schists in the Sanbagawa belt with the appearance of garnet and postulate that the incorporation of Ca in garnet is one of the factors that destabilizes sphene in these rocks.

Sphene has also been reported from biotite gneiss and quartzite (Corfu and Easton, 1997; Harper, 1997; Corfu and Stone, 1998). The biotite gneiss described by Harper (1997) is a semi-pelite, while that described by Corfu and Stone (1998) is described as a metagraywacke. In either instance, the rock must be somewhat more calcic than typical pelitic rocks to host sphene. Likewise, the sphene-bearing quartzite described by (Corfu and Easton, 1997) must be somewhat calcareous.

3.2.4. Orthogneisses

Sphene is found in many metamorphosed granitic rocks (Evans and Patrick, 1987; Patrick, 1995). Many of the reactions producing sphene are similar to those described for mafic rocks (Figs. 2 and 3) but sphene may also be produced from Ti released during the hydration of biotite to chlorite (Ferry, 1979; Studemeister, 1985). Sphene-forming reactions involving the breakdown of biotite and hornblende have also been postulated in shear zones cutting granitic rocks (Gibbons and Horak, 1984).

3.3. Solid solutions in sphene

Natural sphene appears to be a solid solution involving three endmembers, CaTiSiO_5 , CaAlSi -

$\text{O}_4(\text{OH})$, and $\text{CaAlSiO}_4(\text{F})$. Sphene may accommodate as much as 50% of the $\text{CaAlSiO}_5(\text{OH})$ and $\text{CaAlSiO}_5\text{F}$ components; apparently, this solid solution is so important in metamorphic rocks that metamorphic sphene without Al_2O_3 is unknown (Oberti et al., 1991). Although both the $\text{CaAlSiO}_5(\text{OH})$ and $\text{CaAlSiO}_5\text{F}$ components are stabilized by low T and high pressures, sphenes rich in $\text{CaAlSiO}_5(\text{OH})$ are most common in low temperature–low pressure rocks whereas those rich in $\text{CaAlSiO}_5\text{F}$ are most common in high pressure rocks (Enami et al., 1993).

One effect of these solid solutions is to extend the stability of Al, F sphene to much higher pressures than Al-free sphene. This would explain the occurrence of Al, F sphene in high and ultrahigh pressure rocks (Franz and Spear, 1985; Enami et al., 1993; Carswell et al., 1996), conditions where sphene would otherwise not be stable. Because of solid solution, in addition to the discontinuous reactions listed above, there are important continuous metamorphic reactions that involve sphene. This has led Smith (1981) to suggest that the Al content of sphene may be a geobarometer, although such a barometer has not yet been formalized. An example of a continuous reaction in amphibolite would be a reaction between $\text{Al}(\text{OH})$ sphene, ilmenite, and quartz to make anorthite, actinolite, and Ti-sphene (reaction 15). This reaction produces a significant amount of water, suggesting that Al in sphene (at least in amphibolite facies) is controlled by temperature as well as pressure. The assemblage actinolite–plagioclase–quartz–ilmenite–sphene is common in metabasites, and in this assemblage sphene should continually change its composition by reaction (15) to accommodate changes in pressure, temperature, and water activity. This is important in geochronometry because it means that sphene will not be inert but will react to reflect changes in pressure, temperature, or fluid composition. If the multiple growth events in the rock were separated by a significant period of time, then the U–Pb systematics of sphene will be profoundly affected.

3.4. Examples of multi-stage growth

Numerous studies have described metamorphic rocks containing sphene that record multiple growth events. These multiple generations are visible opti-

cally (Franz and Spear, 1985; Tucker et al., 1986; Mezger et al., 1991; Johansson et al., 1993; Kamio et al., 1996; Essex et al., 1997; Pidgeon et al., 1996; Verts et al., 1996; Ketchum et al., 1997; Corfu and Stone, 1998), and in back-scatter electron imaging (Franz and Spear, 1985; Enami et al., 1993). Grains that are richer in Al tend to have lower index of refraction and lower birefringence than Ti-rich sphene (Franz and Spear, 1985), whereas those that are richer in Fe^{3+} tend to be darker in color.

In some rocks, different colors are correlated to distinct age populations and differences in U–Pb systematics (Johansson et al., 1993; Chen and Moore, 1982; Essex et al., 1997; Corfu, 1996; Verts et al., 1996; Kamio et al., 1996; Ketchum et al., 1997; Corfu and Stone, 1998). Perhaps the best documented case is that of Verts et al. (1996), who described the behavior of sphene in the contact aureole of the Laramie Anorthosite Complex. The sphene comes from a series of amphibolites that were metamorphosed under Barrovian metamorphic conditions at 1.76 Ga and then subjected to contact metamorphism at 1.43 Ga in the contact aureole of the Red Mountain pluton. Outside the contact aureole, the amphibolite contains sphene that is brown in thin section (under PPL) and dark brown in grain mounts. Within the aureole, it is overgrown by a

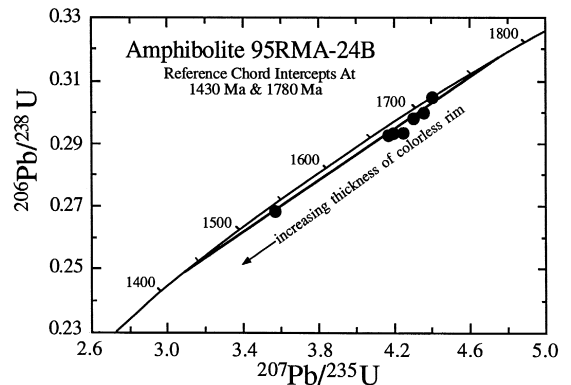


Fig. 6. U–Pb isochron diagram of sphene data from an amphibolite that underwent regional metamorphism at 1780 Ma and contact metamorphism at 1430 Ma. Each sphene grain contains a dark core, presumably formed during regional metamorphism and a light rim that is likely a product of contact metamorphism. Each analysis represents a population with a different proportion of rim to core. Error ellipses are not shown but for most points the symbols are larger than the error ellipse. After Verts et al. (1996).

sphene that is pale brown in thin section and nearly colorless in grain mounts. These overgrowths are found at distances up to 2.4 km from the contact, well outside the limits of contact metamorphism. The U–Pb ages of composite grains become younger with increasing proportion of the pale overgrowths and, because these grains lie on a chord between the age of regional metamorphism and that of contact metamorphism (Fig. 6), Verts et al. (1996) concluded that the two colors represent sphene grains that grew at different times. This implies that a major process by which U–Pb systematics in sphene is reset is due to growth of new sphene, rather than diffusion.

4. U–Pb characteristics of sphene

4.1. Closure T

Even though U–Pb systematics of sphene may be affected by growth of new sphene, it is still important to know the closure temperature for diffusion, since that parameter determines the temperatures at which diffusive resetting becomes more important than mineral growth. The closure temperature for sphene is poorly known. Part of this problem is caused by the fact that closure T is a complex function involving diffusivity (D), effective diffusion radius (which may not be the same as grain size), and cooling rate (Dodson, 1973). Unless noted otherwise, in this discussion we will consider an effective diffusion radius of 0.1 mm (on the small size for most rocks) and a cooling rate of $10^\circ/\text{Ma}$ (typical for an orogenic belt). The closure temperature will be higher for larger grains or grains in more quickly cooled environments.

Early empirical studies suggested that sphene had a closure temperature of around 500°C (see Gascoyne (1986) for summary). These results are based upon studies such as those of Hanson et al. (1971) and Tucker et al. (1986) that determined the temperature at which sphene U–Pb ages reset in metamorphic terranes. Recently, there have been a significant number of studies indicating that sphene may preserve older U–Pb ages even after undergoing high-grade metamorphism. For example, Scott and St. Onge (1995) analyzed sphene of different sizes (1 to

0.075 mm) from rocks that were metamorphosed at high temperatures (660°C – 700°C). These all gave the same U–Pb ages, indicating that they had grown below the closure T for the smallest grains. Studies of sphene from high-grade rocks suggest that the closure T for sphene is $> 650^\circ\text{C}$ (Schärer et al., 1994; Essex et al., 1997) whereas Zhang and Schaerer (1996) and Pidgeon et al. (1996) each described sphene from syenite that retained older U–Pb ages. These authors suggested that the closure temperature is considerably greater than 700°C . In contrast, Verts et al. (1996) report dark sphene cores (presumably grown at 1.78 Ga) that have completely reset in rocks metamorphosed at $T > 700^\circ\text{C}$ in the contact aureole of the Laramie Anorthosite Complex, which suggests that the closure temperature for grains with a diameter of $400\ \mu$ is not far above 700°C .

The studies showing that sphene has not reset at high temperatures are more valuable for estimating closure temperature than the estimates based upon the observed resetting of sphene, because the latter assume that this resetting resulted solely by diffusive processes. As we noted above, sphene is very reactive during metamorphism, and therefore, U–Pb ages are likely to be reset at low temperatures by growth of new sphene, rather than by diffusion. The high closure temperature required by the occurrence of relict U–Pb ages in sphene from high grade terranes is to some extent compatible with theoretical calculations of Dahl (1997) and experimental measurement of Pb diffusion in sphene by Cherniak (1993). By taking the lowest diffusivity allowed within the error range quoted by Cherniak (1993), we calculate a closure T of 660°C for grains with 0.1 mm radius of diffusion and a $10^\circ\text{C}/\text{Ma}$ cooling rate, not far from that suggested by Scott and St. Onge (1995). A cooling rate of $100^\circ\text{C}/\text{Ma}$ for the same grain yields closure temperature of around 700°C , not far from that estimated for grains included in syenite (Zhang and Schaerer, 1996; Pidgeon et al., 1996).

The evidence noted above indicates that the closure temperature for sphene, even for small grains in slowly cooled rocks, is above 660°C , and possibly above 700°C . Thus, for the pressures typical of regional metamorphism, the closure temperature for sphene is above that of the wet granite solidus. This means that sphene grown in amphibolite facies (or lower) or during deuteric alteration of granites will

have recorded the U–Pb age of crystallization, rather than that at which the mineral closed to diffusion. This makes sphene a key mineral for dating metamorphism and deformation at medium to high temperatures.

4.2. U–Pb abundances in natural sphene

The initial U content of sphene from most igneous rocks ranges from 20 to 1000 ppm, with the highest reported values being more than 3000 ppm in sphene from leucosomes in granulite-facies rocks (Timmermann et al., 1997) (Fig. 7A). Common Pb tends to run from 0.2 to 10 ppm. There is little distinction between U and Pb contents of sphene from different rock types, although some aplites and pegmatites extend down to low U contents. The variation in U and Pb within sphene from each rock type is large and the fields are overlapping, hiding any within-pluton variation caused by differentiation. The few studies that have enough data from single batholiths do show distinct variations in U and Pb content of sphene with rock composition. For example, common Pb and initial U in sphene decrease from granodiorite to quartz monzonite to granite in the Sierra Nevada (Chen and Moore, 1982), possibly in response to differentiation. There is also a clear decrease in common Pb with decreasing initial U in Acadian granites in eastern Quebec described by

Simonetti and Diog (1990), although it is not as closely tied to composition as is the trend in the Sierra Nevada.

Sphene from orthogneisses has similar composition to that from magmatic rocks (Fig. 7B), but it is unclear how much of the range represents the composition of sphene in the igneous protolith. There is

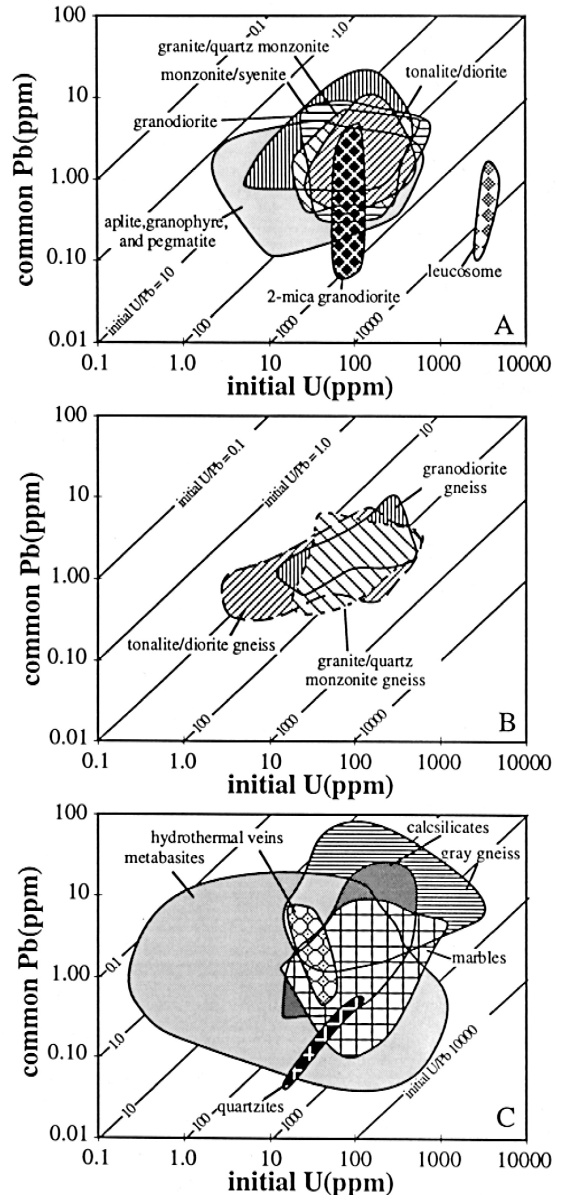


Fig. 7. Calculated common Pb and U compositions from sphene described in the literature. Initial U is calculated from present day U ppm adjusted for age. Common Pb represents common non-radiogenic Pb incorporated in sphene. Light lines represent contours of initial U/Pb. Measured $^{206}\text{Pb}/^{204}\text{Pb}$ and corresponding dependence of calculated age on the choice of initial Pb isotopic composition will be affected by both the initial U/Pb value and the age of the sample, see text for discussion. (A) Sphene from igneous rocks, aplite, granophyre, and pegmatite (22 points), granodiorite (64 points), granite/quartz monzonite (55 points), leucosome (3 points), monzonite/syenite (34 points), tonalite/diorite (40 points), two-mica granodiorite (4 points). (B) Sphene from granite/quartz monzonite gneiss (16 points), granodiorite gneiss (13 points) and tonalite/diorite gneiss (60 points). (C) Sphene from metamorphic rocks: calcilicite rocks (49 points), gray gneiss (13 points), hydrothermal veins (10 points), marbles (38 points), metabasites (85 points), and quartzite (3 points). Sources of data are given in Appendix A.

evidence that metamorphic sphene is less enriched in common Pb and initial U than that from magmatic rocks, although this is not conclusively demonstrated in Fig. 7B. However, it is particularly well displayed in the data of Corfu and Stone (1998), who found pale, metamorphic sphene rimming dark magmatic sphene in orthogneisses, with the pale sphene having markedly lower U and Pb than the dark sphene.

Sphene from marbles are distinctly enriched in initial U, with up to 1000 ppm, and poor in common Pb (most samples have 2 ppm or less) (Fig. 7C). Sphene from calc-silicates have similar values, although they may not be as U-rich and a sizable proportion are richer in common Pb. Sphene from the few samples of biotite gneiss available have a wide range of composition, but most are relatively rich in common Pb and U. The three samples of sphene in quartzite reported by Corfu and Easton (1997) have less than 1 ppm common Pb and less than 100 ppm initial U. Sphene from metabasites, including mafic gneiss, amphibolitized diabase dikes, and metabasalts, have a wide range in compositions, some of which are so low in U and rich in common Pb that they are unusable for dating. Part of this seems to be due to metamorphic grade, for the sphene from low-amphibolite facies and greenschist facies metabasites reported by Harper (1997) have a too low U/Pb ratio to provide a reasonable date. It is difficult to determine the extent to which the sphene U/Pb composition is dependent on metamorphic grade, because few geochronologists report analyses for minerals that cannot be used for dating. However, Mattinson (1986), who studied sphene from blueschists, states that many of the grains he analyzed have very low $^{206}\text{Pb}/^{204}\text{Pb}$ ratios and could not be used for chronology.

5. Conclusions — sphene as a geochronometer

From the discussion above, two points are important when considering the role of sphene as a geochronometer. First is that sphene is a relatively reactive mineral and the abundance and composition of sphene in a rock will change to reflect changes in pressure, temperature, and composition of the fluid phase. For this reason, sphene in a rock that underwent a complicated thermal history may contain

multiple generations of sphene that will show complex U–Pb systematics (Verts et al., 1996; Corfu and Stone, 1998). If the various generations of sphene were not visible optically, the U–Pb results may be difficult to interpret. The second important observation is that sphene has a high closure temperature (possibly as high as 700°C), which means that the U–Pb ages of sphene in most metamorphic rocks will reflect that time that the sphene grew, rather than a closure temperature. This means that, given independent evidence for the time of crystal growth, sphene has the potential of being a powerful tool not only for dating igneous events, but also for determining the age of hydrothermal, metamorphic, and deformational processes.

5.1. Analytical considerations

Sphene records a wide range of initial U/Pb ratios from 0.1 to 30,000 (Fig. 7). If the sphene is young, or its initial U/Pb concentration is low, the blank-corrected $^{206}\text{Pb}/^{204}\text{Pb}$ will be low, proportion of common Pb high, and plotting strategies and the choice of initial Pb isotopic composition will have a significant effect on the calculated ages. Conversely, if the sphene is old or the initial U/Pb is high, these effects will be minimal. For example, for Mesoproterozoic samples (1.43 Ga in this case), an initial U/Pb of 10 will produce a measured $^{206}\text{Pb}/^{204}\text{Pb}$ of 100 and a corresponding range of 10 Ma in the calculated $^{206}\text{Pb}/^{206}\text{Pb}$ age for geologically reasonable initial Pb isotopic compositions (Verts et al., 1996). For Mesozoic-aged samples, an initial U/Pb of 100 is required to produce a measured $^{206}\text{Pb}/^{204}\text{Pb}$ of 100 and comparable fractional dependence of the age on choice of initial composition.

Depending on the proportion of initial Pb, there are a variety of strategies for extracting useful radiometric information from sphene U–Pb data. For samples with blank-corrected $^{206}\text{Pb}/^{204}\text{Pb}$ of 300 or more, the proportion of initial Pb is less than 10% of total Pb and the choice of initial Pb isotopic composition will have only a slight effect on calculated ages. Either model Pb compositions (e.g. Stacey and Kramers, 1975) or measured isotopic compositions of coexisting low-U phases can be used to reduce data for plotting on a standard concordia diagram. For samples with blank-corrected $^{206}\text{Pb}/^{204}\text{Pb}$ of

300 to 60, we recommended concordia plots of data reduced with measured Pb isotopic compositions of coexisting low-U phases, such as alkali feldspar or calcite. Alkali feldspar is well-suited, as the diffusion characteristics of Pb are very similar for sphene and feldspar (Cherniak, 1995), so in high temperature applications, the two phases are likely to have reached isotopic equilibration prior to closure of Pb diffusion in sphene. Calcite is useful for metamorphosed carbonates and calc-silicates, but any low-U phase could be used if the phase was produced at the same time as sphene or participated in the sphene-forming reaction. For samples with blank-corrected $^{206}\text{Pb}/^{204}\text{Pb}$ of less than 60, more than 50% of the Pb in the sphene will be common Pb and it is critical that there is independent evidence for initial Pb isotopic equilibration of all phases used in calculating concordia coordinates, as these are truly multi-phase ages. For some sphene samples, especially from weakly metamorphosed mafic rocks that contain very low initial U/Pb ratios, the radiogenic signal may be too small to interpret (Mattinson, 1986; Harper, 1997).

The Pb/Pb and U–Pb isochron plots are potentially useful alternatives to concordia diagrams, especially for low $^{206}\text{Pb}/^{204}\text{Pb}$ samples, as they avoid the need for choosing an initial Pb isotopic composition. Isochron plots yield reliable ages only if there are four or more analyses with sufficient spread to regress a line confidently, the analyzed sphene come from a single age population without overgrowths, and the ages are concordant with closed-system isotopic behavior. In light of the evidence for multiple periods of sphene growth presented in this paper, concordia plots are recommended over isochron plots so that potential mixtures of multiple-age growths can be identified and quantified. Planar fits on three-dimensional total-Pb plotting schemes (Ludwig, 1994; Zheng, 1992) have the potential of generating concordia intercepts without assigning an initial Pb isotopic composition, but require sufficient spread of data to define a meaningful plane and are often only useful when the radiogenic data are combined with data from low-U phases (Ludwig, 1994; Chamberlain and Bowring, 2000).

Pb–Pb step leaching method (Frei and Kamber, 1995) has the potential to be very powerful for sphene dating as it appears to fractionate initial Pb from radiogenic Pb and produce high $^{206}\text{Pb}/^{204}\text{Pb}$

ratios in the later leach steps. The process may involve stripping divalent initial Pb from the Ca site in the early steps and slowly releasing tetravalent radiogenic Pb from a silica-gel-like leach front in the later steps (Frei et al., 1997). The resulting Pb isotopic data are often collinear on Pb–Pb isochron plots with a broad spread in data ($^{206}\text{Pb}/^{204}\text{Pb}$ ratios of 30 or so for the early steps, several hundred in the later steps) and resulting age uncertainties of 1% (Frei and Kamber, 1995; Kamber et al., 1995, 1996; Holzer et al., 1998). The chief limitation and disadvantage to the step leaching method is that U is fractionated from Pb, thereby sacrificing the power of U–Pb concordia diagrams to identify and quantify multiple growths or younger disturbances. Pb–Pb step leaching may produce reliable results for single growths of sphene when there is independent evidence for isotopic closure, but it will not be useful for extracting geochronologic information from any complex, multi-stage systems.

5.2. *Strategies for dating*

5.2.1. *Dating of igneous events*

Sphene has long been used to date the age of igneous intrusions (for example, Chen and Moore, 1982; Corfu et al., 1985; Bevier and Whalen, 1990). Because magmatic sphene may have crystallized above its closure temperature, if the pluton was slowly cooled, the sphene age may be a closure age that is somewhat younger than the true magmatic age (Aleinikoff et al., 1993). Because sphene is likely to be produced by any retrogressive reaction, to be certain that the age is not dating a later retrogression that is neither related to the age of emplacement nor to cooling, one should take care to be sure that the sphene in the rock clearly grew at the time the rock crystallized. Such evidence includes igneous textures, such as inclusion of euhedral sphene by clearly igneous minerals such as hornblende or the preservation of euhedral magmatic zoning in sphene (best seen in backscattered images, Fig. 8). Furthermore, igneous sphene is likely to be richer in REEs than secondary sphene, because REEs will be sequestered into minor phases in the rock during igneous crystallization and are not likely to be remobilized during subsequent metamorphic reactions.

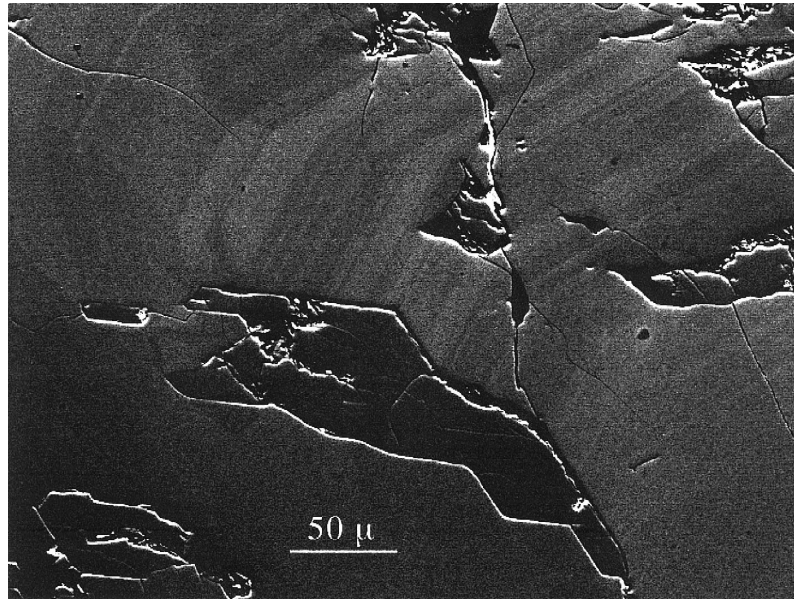


Fig. 8. BSE image showing oscillatory zoning in sphenes from the Sherman Granite. Q = quartz inclusions. Sample 90PH1. For details about this sample, see Frost et al. (1999).

5.2.2. Dating deformation and metamorphism

Because of the reactive nature of sphene, its wide range of stability, and high closure temperature, it is an ideal mineral to use in dating metamorphism. Furthermore, because most metamorphism is associated with deformation, sphene can also be used for dating deformation in medium to high grade terranes. Sphene could be used to date the age of metamorphism and deformation if one can prove that the mineral grew during the metamorphic or deformation event. Preferred rock types in order of decreasing U/Pb ratio are impure marble, calc-silicate, quartzofeldspathic gneiss, and metabasite. As noted above, sphene from low-grade metabasites may have U/Pb ratios that are too low for use as geochronometers. Therefore, in low-grade terranes one should concentrate on sphene from rocks that are richer in U than typical metabasites, such as marbles, dioritic or granitic gneisses or metamorphosed greywacke. Because epidote has lower U and much higher common Pb than coexisting with sphene (Zaldugui et al., 1996), it may also be possible to obtain sphene with a favorable U/Pb ratio from a low-temperature epidote-rich metabasite. In such a rock, the epidote may

have sequestered Pb, increasing the U/Pb ratio of the sphene.

To evaluate the significance of the age obtained, one must be certain that the sphene grew during the event in question. This can be done in several ways. One method is to show that sphene in a rock lies parallel to lineations or foliations that clearly formed during the metamorphism or deformation in question (Getty and Gromet, 1992; Resor et al., 1996). Another way would be to show that a reaction relation exists between sphene and the other phases in a rock and to demonstrate that this reaction was operating at the time of metamorphism. Perhaps the most unambiguous approach is to show that sphene is found in a rock that contained no sphene previous to the metamorphic or deformation event (Resor et al., 1996). An elegant example of this was described by Cliff et al. (1993) who dated the Dalradian metamorphism using sphene collected from a calc-silicate horizon that lay between a metapelite layer and a marble. Since the calc-silicate horizon formed by metasomatism during the metamorphism, the sphene obviously could not have existed prior to the metamorphism.

5.2.3. Dating hydrothermal activity

Sphene could be used to date the age of hydrothermal activity associated with ore deposits. Because CaO is leached from the most acidic environments, such dating can be applied to only a small subset of ore deposits. This includes areas of propylitic alteration, where Ca-rich minerals such as epidote, calcite, and sphene are stable (Meyer and Hemley, 1967), skarn, and areas of carbonatization associated with gold deposits. It is in the later type of deposit that sphene dating has been used most extensively (Jamielita et al., 1990; Zweng et al., 1993; Abraham et al., 1994).

5.3. Summary

Sphene has been long used as a geochronometer in igneous rocks. Recent work has led to the recognition that the U–Pb systematics of sphene are more likely to be controlled by metamorphic growth than by diffusion. This, in addition to the fact that the U–Pb system in sphene has a closure temperatures near the upper limits of amphibolite facies means that in addition to dating igneous events, sphene can also be a valuable geochronometer to date metamorphism and deformation in high-grade terranes. To do so, one needs to integrate geochronology with the use of microtextures, which will allow one to identify the metamorphic reactions by which sphene grew as well as the relation of sphene to the dominant fabric elements in the rock.

Acknowledgements

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Appendix A. References used for Fig. 7

Abraham et al., 1994; Aleinikoff et al., 1993; Ayer and Davis, 1997; Barr et al., 1990; Barrie, 1990; Barth et al., 1997; Bevier and Whalen, 1990; Bevier et al., 1990; Bosch et al., 1996; Camilleri and Chamberlain, 1997; Carr, 1995; Chen et al., 1995;

Chen and Moore, 1982; Cliff et al., 1993; Corfu, 1980, 1988; Corfu and Easton, 1997; Corfu and Grunsky, 1987; Corfu et al., 1985, 1994; Corfu and Muir, 1989; Corfu and Stone, 1998; Corfu and Stott, 1986, 1993a,b; Davis and Bartlett, 1988; Davis et al., 1989, 1995; Dubé et al., 1996; Dunning et al., 1990; Dunning and O'Brien, 1989; Dusel-Bacon and Aleinikoff, 1996; Essex et al., 1997; Friedman and Martignole, 1995; Gower et al., 1991; Harper, 1997; Hirdes et al., 1996; Hoisch et al., 1997; Jamielita et al., 1990; Johansson et al., 1993; Johnston et al., 1996; Kerr et al., 1992; Ketchum et al., 1997; Mezger et al., 1991, 1993; Miller et al., 1996; Moecher et al., 1997; Mortensen, 1993a,b; Mortensen and Card, 1993; Mortensen and Ciesielski, 1987; Mortensen et al., 1987; Nemchin et al., 1994; Resor et al., 1996; Romer and Nisca, 1995; Schaltegger and Corfu, 1992; Schaltegger et al., 1996; Schärer et al., 1994; Scott and Machado, 1995; Scott and St-Onge, 1995; Simonetti and Diog, 1990; Timmermann et al., 1997; Tucker et al., 1986, 1990; Verts et al., 1996; von Blackenburg, 1992; Wintsch and Aleinikoff, 1987; Zalduegui et al., 1996; Zweng et al., 1993.

References

- Abraham, A.P.G., Davis, D.W., Kamio, S.L., Spooner, E.T.C., 1994. Geochronological constraints on late Archean magmatism deformation and gold-quartz vein mineralization in the northwestern Anialik River greenstone belt and igneous complex, Slave Province, N.W.T. *Can. J. Earth Sci.* 31, 1365–1383.
- Aleinikoff, J.N., Moore, T.E., Walter, M., Nokleberg, W.J., 1993. U–Pb ages of zircon, monazite, and sphene from Devonian metagranites and metafelsites central Brooks Range, Alaska. *U.S. Geol. Surv. Bull.*, B 2068, 59–70.
- Ayer, J.A., Davis, D.W., 1997. Neoproterozoic evolution of differing convergent margin assemblages in the Wabigoon Subprovince: geochemical and geochronological evidence from the Lake of the Woods greenstone belt, Superior province, Northwestern Ontario. *Precambrian Res.* 81, 155–178.
- Baltatzis, E.G., Katagas, C.G., 1984. The pumpellyite-actinolite and contiguous facies in part of the Phyllite–Quartzite Series, central Northern Peloponnesus, Greece. *J. Metamorph. Geol.* 2, 349–363.
- Barr, S.M., Dunning, G.R., Raeside, R.P., Jamieson, R.A., 1990. Contrasting U–Pb ages from plutons in the Bras d'Or and Mira terranes of Cape Breton Island, Nova Scotia. *Can. J. Earth Sci.* 27, 1200–1208.
- Barrie, C.T., 1990. U–Pb garnet and titanite age for the Bristol Township lamprophyre suite, western Abitibi subprovince, Canada. *Can. J. Earth Sci.* 27, 1451–1456.

- Barth, A.P., Tosdal, R.M., Wooden, J.L., Howard, K.A., 1997. Triassic plutonism in southern California: southward younging of arc initiation along a truncated continental margin. *Tectonics* 16, 290–304.
- Begin, N.J., 1990. Plagioclase immiscibility and Ti-minerals relationships in metabasites of the Cape Smith Belt, northern Quebec. *Geol. Assoc. Can. Program Abstracts* 15, A8.
- Begin, N.J., 1992. Contrasting mineral isograd sequences in metabasites of the Cape Smith Belt, northern Quebec, Canada: three new bathograds for mafic rocks. *J. Metamorph. Geol.* 10, 685–704.
- Beiersdorfer, R.E., 1993. Metamorphism of a Late Jurassic volcano-plutonic arc, northern California, USA. *J. Metamorph. Geol.* 11, 415–428.
- Berman, R.G., 1988. Internally-consistent thermodynamic data for minerals in the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{MgO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{TiO}_2-\text{H}_2\text{O}-\text{CO}_2$. *J. Petrol.* 29, 445–522.
- Bevier, M.L., Whalen, J.B., 1990. U–Pb geochronology of Silurian granites, Miramichi Terrane, New Brunswick. *Pap.-Geol. Surv. Can.* 89-2, 93–100.
- Bevier, M.L., White, C.E., Barr, S.M., 1990. Late Precambrian U–Pb ages for the Brookville gneiss, southern New Brunswick. *J. Geol.* 98, 955–965.
- Bosch, D., Bruguier, O., Pidgeon, R.T., 1996. Evolution of an Archean metamorphic belt: a conventional and SHRIMP U–Pb study of accessory minerals from the Jimperding Metamorphic Belt, Yilgarn Craton, West Australia. *J. Geol.* 104, 695–711.
- Boundy, T.M., Mezger, K., Essene, E.J., 1997. Temporal and tectonic evolution of the granulite–eclogite association from the Bergen Arcs, western Norway. *Lithos* 39, 159–178.
- Camilleri, P.A., Chamberlain, K.R., 1997. Mesozoic tectonics and metamorphism in the Pequop Mountains and Wood Hills region, northeast Nevada: implications for the architecture and evolution of the Sevier orogen. *Geol. Soc. Am. Bull.* 109, 74–94.
- Carmichael, D.M., 1970. Intersecting isograds in the Whetstone Lake area, Ontario. *J. Petrol.* 11, 147–181.
- Carr, S.D., 1995. The southern Omineca Belt, British Columbia: new perspectives from the Lithoprobe Geoscience Program. *Can. J. Earth Sci.* 32, 1720–1739.
- Carswell, D.A., Wilson, R.N., Zhai, M., 1996. Ultra-high pressure aluminous titanites in carbonate-bearing eclogites at Shuanghe in Dabieshan, central China. *Mineral. Mag.* 60, 461–471.
- Cassidy, K.F., Groves, D.I., 1988. Manganian ilmenite formed during regional metamorphism of Archean mafic and ultramafic rocks from Western Australia. *Can. Mineral.* 26, 999–1012.
- Castelli, D., 1991. Eclogitic metamorphism in carbonate rocks: the example of impure marbles from the Sesia-Lanzo Zone, Italian Western Alps. *J. Metamorph. Geol.* 9, 61–77.
- Cérny, P., Novak, M., Chapman, R., 1995. The $\text{Al}(\text{Nb,Ta})\text{Ti}_{-2}$ substitution in titanite: the emergence of a new species? *Mineral. Petrol.* 52, 61–73.
- Chamberlain, K.R., Bowring, S.A., 2000. Apatite-feldspar U–Pb thermochronometer: a reliable mid-range ($\sim 450^\circ\text{C}$), diffusion-controlled system. *Chem. Geol.* this issue.
- Chen, J.H., Moore, J.G., 1982. Uranium–lead isotopic ages from the Sierra Nevada batholith, California. *J. Geophys. Res.* 87, 4761–4784.
- Chen, Y.D., Krogh, T.E., Lumbers, S.B., 1995. Neoproterozoic trondhjemitic and tonalitic orthogneiss identified within the northern Grenville Province in Ontario by precise U–Pb dating and petrologic studies. *Precambrian Res.* 72, 263–281.
- Cherniak, D.J., 1993. Lead diffusion in titanite and preliminary results on the effects of radiation damage on Pb transport. *Chem. Geol.* 110, 177–194.
- Cherniak, D.J., 1995. Diffusion of lead in plagioclase and K-feldspar, an investigation using Rutherford backscattering and resonant nuclear reaction analysis. *Contrib. Mineral. Petrol.* 120, 358–371.
- Cliff, R.A., Yardley, B.W.D., Bussy, F., 1993. U–Pb isotopic dating of fluid infiltration and metasomatism during Dalradian regional metamorphism in Connemara, western Ireland. *J. Metamorph. Geol.* 11, 185–191.
- Corfu, F., 1980. U–Pb and Rb–Sr systematics in a polyorogenic segment of the Precambrian shield, central southern Norway. *Lithos* 13, 305–323.
- Corfu, F., 1988. Differential response of U–Pb systems in coexisting accessory minerals, Winnipeg River Subprovince, Canadian Shield: implications for Archean crustal growth and stabilization. *Contrib. Mineral. Petrol.* 98, 312–325.
- Corfu, F., 1996. Multistage zircon and titanite growth and inheritance in an Archean gneiss complex, Winnipeg River Subprovince, Ontario. *Earth Planetary Sci. Lett.* 141, 175–186.
- Corfu, F., Krogh, T.E., Ayres, L.D., 1985. U–Pb zircon and sphene geochronology of a composite Archean granitoid batholith, Favorable Lake area, northwestern Ontario. *Can. J. Earth Sci.* 22, 1436–1451.
- Corfu, F., Stott, G.M., 1986. U–Pb ages for late magmatism and regional deformation in the Shebandowan belt, Superior Province, Canada. *Can. J. Earth Sci.* 23, 1075–1082.
- Corfu, F., Grunsky, E.C., 1987. Igneous and tectonic evolution of the Batchawana greenstone belt, Superior province: a U–Pb zircon and titanite study. *J. Geol.* 95, 87–105.
- Corfu, F., Muir, T.L., 1989. The Hemlo–Heron Bay greenstone belt and Hemlo Au–Mo deposit, Superior Province, Ontario, Canada: 2. Timing of metamorphism, alteration and Au mineralization from titanite, rutile, and monazite U–Pb geochronology. *Chem. Geol.* 79, 201–223.
- Corfu, F., Stott, G.M., 1993a. Age and petrogenesis of two Late Archean magmatic suites, northwestern Superior Province, Canada: zircon U–Pb and Lu–Hf isotopic relations. *J. Petrol.* 34, 817–838.
- Corfu, F., Stott, G.M., 1993b. U–Pb geochronology of the central Uchi subprovince, Superior Province. *Can. J. Earth Sci.* 30, 1179–1196.
- Corfu, F., Heaman, L.M., Rogers, G., 1994. Polymetamorphic evolution of the Lewisian complex, NW Scotland, as recorded by U–Pb isotopic compositions of zircon, titanite and rutile. *Contrib. Mineral. Petrol.* 117, 215–228.
- Corfu, F., Easton, R.M., 1997. Sharbot Lake terrane and its relationships to the Frontenac terrane, Central Metasedimentary Belt, Grenville Province: new insights from U–Pb geochronology. *Can. J. Earth Sci.* 34, 1239–1257.
- Corfu, F., Stone, D., 1998. The significance of titanite and apatite

- U–Pb ages: constraints for the post-magmatic thermal–hydrothermal evolution of a batholithic complex, Berens River area, northwestern Superior Province, Canada. *Geochim. Cosmochim. Acta* 62, 2979–2995.
- Dahl, P.S., 1997. A crystal-chemical basis for Pb retention and fission-track annealing systematics in U-bearing minerals, with implications for geochronology. *Earth Planetary Sci. Lett.* 150, 277–290.
- Dasgupta, S., 1993. Contrasting mineral parageneses in high-temperature calc-silicate granulites: examples from the Eastern Ghats, India. *J. Metamorph. Geol.* 11, 193–202.
- Davis, D.W., Bartlett, J.R., 1988. Geochronology of the Belmont Lake metavolcanic complex and implications for crustal development in the Central Metasedimentary belt, Grenville Province, Ontario. *Can. J. Earth Sci.* 25, 1751–1759.
- Davis, D.W., Poulsen, K.H., Kamo, S.L., 1989. New insights into Archean crustal development from geochronology in the Rainy Lake area, Superior Province, Canada. *J. Geol.* 97, 379–398.
- Davis, W.J., Machado, N., Gariépy, C., Swayer, E.W., Benn, K., 1995. U–Pb geochronology of the Opatca tonalite–gneiss belt and its relationship to the Abitibi greenstone belt, Superior Province, Quebec. *Can. J. Earth Sci.* 32, 113–127.
- Deer, W.A., Howie, R.A., Zussman, J., 1982. Rock forming minerals. *Orthosilicates* vol. 1A. Longman, London.
- Dodson, M.H., 1973. Closure temperature in cooling geochronological and petrological systems. *Contrib. Mineral. Petrol.* 40, 259–274.
- Dubé, B., Dunning, G.R., Lauzière, K., Roddick, J.C., 1996. New insights into the Appalachian Orogen from geology and geochronology along the Cape Ray fault zone, southwest Newfoundland. *Geol. Soc. Am. Bull.* 108, 101–116.
- Dunning, G.R., O'Brien, S.J., 1989. Later Proterozoic–early Paleozoic crust in the Hermitage flexure, Newfoundland Appalachians: U/Pb ages and tectonic significance. *Geology* 17, 548–551.
- Dunning, G.R., Barr, S.M., Raeside, R.P., Jamieson, R.A., 1990. U–Pb zircon, titanite, and monazite ages in the Bras d'Or and Aspy terranes of Cape Breton Island, Nova Scotia: implications for igneous and metamorphic history. *Geol. Soc. Am. Bull.* 102, 322–330.
- Dusel-Bacon, C., Aleinikoff, J.N., 1996. U–Pb zircon and titanite ages for augen gneiss from the Divide Mountain area, eastern Yukon-Tanana upland, Alaska, and evidence for the composite nature of the Fifymile batholith. *U.S. Geol. Surv. Bull.* 2152, 131–141.
- El-Shazly, A.E.K., 1994. Petrology of lawsonite-pumpellyite- and sodic amphibole-bearing metabasites from north-east Oman. *J. Metamorph. Petrol.* 12, 23–48.
- Enami, M., 1983. Petrology of pelitic schists in the oligoclase-biotite zone of the Sanbagawa metamorphic terrane, Japan: phase equilibria in the highest grade zone of a high-pressure intermediate type of metamorphic belt. *J. Metamorph. Geol.* 1, 141–161.
- Enami, M., Suzuki, K., Liou, J.G., Bird, D.K., 1993. Al–Fe³⁺ and F–OH substitutions in titanite and constraints on their P–T dependence. *Eur. J. Mineral.* 5, 219–231.
- Essex, R.M., Gromet, L.P., Andréasson, P.-G., Albrecht, L., 1997. Early Ordovician U–Pb metamorphic ages of the eclogite-bearing Seve Nappes, Northern Scandinavian Caledonides. *J. Metamorph. Geol.* 15, 665–676.
- Evans, B.W., 1990. Phase relations of epidote-blueschists. *Lithos* 25, 3–23.
- Evans, B.W., Patrick, B.E., 1987. Phengite-3T in high-pressure metamorphosed granitic orthogneiss, Seward Peninsula, Alaska. *Can. Mineral.* 25, 141–158.
- Ferry, J.M., 1979. Reaction mechanisms, physical conditions and mass transfer during hydrothermal alteration of mica and feldspar in granitic rocks from south-central Maine, USA. *Contrib. Mineral. Petrol.* 68, 125–139.
- Ferry, J.M., 1984. A biotite isograd in South-Central Maine, U.S.A.: mineral reactions, fluid transfer, and heat transfer. *J. Petrol.* 25, 871–893.
- Force, E.R., 1976. Metamorphic source rocks of titanium placer deposits — a geochemical cycle. *U.S. Geol. Surv. Prof. Pap.* 959-B.
- Force, E.R., 1991. Geology of titanium-mineral deposits. *Spec. Pap.-Geol. Soc. Am.* 259.
- Franz, G., Spear, F.S., 1985. Aluminous titanite (sphene) from the eclogite zone, South-central Tauern Window, Austria. *Chem. Geol.* 50, 33–46.
- Frei, R., Kamber, B.S., 1995. Single mineral Pb–Pb dating. *Earth Planetary Sci. Lett.* 129, 261–268.
- Frei, R., Villa, I.M., Nägler, Th.F., Kramers, J.D., Przybyłowicz, W.J., Prozesky, V.M., Hofmann, B.A., Kamber, B.S., 1997. Single mineral dating by the Pb–Pb step-leaching method: assessing the mechanisms. *Geochim. Cosmochim. Acta* 61, 393–414.
- Friedman, R.M., Martignole, J., 1995. Mesoproterozoic sedimentation, magmatism, and metamorphism in the southern part of the Grenville Province (western Quebec): U–Pb geochronological constraints. *Can. J. Earth Sci.* 32, 2103–2114.
- Frost, B.R., 1991. Oxide minerals in metamorphic rocks. *Rev. Mineral.* 25, 469–487.
- Frost, B.R., Lindsley, D.H., 1991. Occurrence of iron–titanium oxide minerals in igneous rocks. *Rev. Mineral.* 25, 433–486.
- Frost, C.D., Frost, B.R., Chamberlain, K.R., Edwards, B.R., 1999. Petrogenesis of the 1.43 Ga Sherman batholith, SE Wyoming: a reduced rapakivi-type anorogenic granite. *J. Petrol.* 40, 1771–1802.
- Gascoyne, M., 1986. Evidence for the stability of potential nuclear waste host, sphene, over geological time, from uranium–lead ages and uranium series disequilibrium measurements. *Appl. Geochem.* 1, 199–210.
- Getty, S.R., Gromet, L.P., 1992. Geochronological constraints on ductile deformation, crustal extension, and doming around a basement-cover boundary, New England Appalachians. *Am. J. Sci.* 292, 359–397.
- Ghent, E.D., DeVries, C.D.S., 1972. Plagioclase-garnet-epidote equilibria in hornblende-plagioclase bearing rocks from the Esplande Range, British Columbia. *Can. J. Earth Sci.* 9, 618–635.
- Ghent, E.D., Stout, M.Z., Erdmer, P., 1993. Pressure–temperature evolution of lawsonite-bearing eclogites, Pinchi Lake, British Columbia. *J. Metamorph. Geol.* 11, 279–290.

- Gibbons, W., Horak, J., 1984. Alpine metamorphism of Hercynian hornblende granodiorite beneath the blueschist facies *schistes lustrés* nappe of NE Corsica. *J. Metamorph. Geol.* 2, 95–113.
- Gower, C.F., Heaman, L.M., Loweridge, W.D., Schärer, U., Tucker, R.D., 1991. Grenvillian magmatism in the eastern Grenville province, Canada. *Precambrian Res.* 51, 315–336.
- Hanson, G.N., Catanzaro, E.J., Anderson, D.H., 1971. U–Pb ages for titanite in a contact metamorphic zone. *Earth Planetary Sci. Lett.* 12, 231–237.
- Harper, K.M., 1997. U–Pb age constraints on the timing and duration of Proterozoic and Archean metamorphism along the southern margin of the Archean Wyoming craton. Ph.D. Thesis, University of Wyoming, Laramie, Wyoming.
- Hellman, P.L., Green, T.H., 1979. The role of sphene as an accessory phase in the high-pressure partial melting of hydrous mafic compositions. *Earth Planetary Sci. Lett.* 42, 191–201.
- Higgins, J.B., Ribbe, P.H., 1976. The crystal chemistry and space groups of natural and synthetic titanites. *Am. Mineral.* 61, 878–888.
- Hirdes, W., Davis, D.W., Lüdtke, G., Konan, G., 1996. Two generations of Birimian (Paleoproterozoic) volcanic belts in northeastern Côte d'Ivoire (West Africa): consequences for the Birimian controversy. *Precambrian Res.* 80, 173–191.
- Hoisch, T.D., Heizler, M.T., Zartman, R.E., 1997. Timing of detachment faulting in the Bullfrog Hills and Bare Mountain area, southwest Nevada: inferences from $^{40}\text{Ar}/^{39}\text{Ar}$, K–Ar, U–Pb, and fission track thermochronology. *J. Geophys. Res.* 102, 2815–2833.
- Holzer, L., Frei, R., Barton, J.M. Jr., Kramers, J.D., 1998. Unraveling the record of successive high grade events in the Central Zone of the Limpopo Belt using Pb single phase dating of metamorphic minerals. *Precambrian Res.* 87, 87–115.
- Honegger, K., Le Fort, P., Mascle, G., Zimmermann, J.-L., 1989. The blueschists along the Indus suture zone in Ladakh, NW Himalaya. *J. Metamorph. Geol.* 7, 57–72.
- Hunt, J.A., Kerrick, D.M., 1977. The stability of sphene: experimental redetermination and geologic implications. *Geochim. Cosmochim. Acta* 41, 279–288.
- Itaya, T., Banno, S., 1980. Paragenesis of titanium-bearing accessories in pelitic schists of the Sanbagawa metamorphic belt, Central Shikoku, Japan. *Contrib. Mineral. Petrol.* 73, 267–276.
- Jamielita, R.A., Davis, D.W., Krogh, T.E., 1990. U–Pb evidence for Abitibi gold mineralization postdating greenstone magmatism and metamorphism. *Nature* 346, 331–333.
- Johansson, A., Meier, M., Oberli, F., Wikman, H., 1993. The early evolution of the Southwest Swedish Gneiss Province: geochronological and isotopic evidence from southernmost Sweden. *Precambrian Res.* 64, 361–388.
- Johnston, S.T., Mortensen, J.K., Erdmer, P., 1996. Igneous and metaigneous age constraints for the Aishihik metamorphic suite, southwest Yukon. *Can. J. Earth Sci.* 33, 1543–1555.
- Kamber, B.S., Blenkinsop, T.G., Villa, I.M., Dahl, P.S., 1995. Proterozoic transpressive deformation in the Northern Marginal Zone, Limpopo Belt, Zimbabwe. *J. Geol.* 103, 493–508.
- Kamber, B.S., Biino, G.G., Wijbrans, J.R., Davies, G.R., Villa, I.M., 1996. Archean granulites of the Limpopo Belt, Zimbabwe: One slow exhumation or two rapid events. *Tectonics* 15, 1414–1430.
- Kamio, S.L., Wasteneys, H., Gower, C.F., Krogh, T.E., 1996. U–Pb geochronology of Labradorian and later events in the Grenville Province, eastern Labrador. *Precambrian Res.* 80, 239–260.
- Kerr, A., Krogh, T.E., Corfu, F., Schärer, U., Gandhi, S.S., Kwok, Y.Y., 1992. Episodic Early Proterozoic granitoid plutonism in the Makkovik Province, Labrador: U–Pb geochronological data and geological implications. *Can. J. Earth Sci.* 29, 1166–1179.
- Ketchum, J.W.F., Culshaw, N.G., Dunning, G.R., 1997. U–Pb geochronologic constraints on Paleoproterozoic orogenesis in the northwestern Makkovik Province, Labrador, Canada. *Can. J. Earth Sci.* 34, 1072–1088.
- Klemd, R., Matthes, S., Schüssler, U., 1994. Reaction textures and fluid behavior in very high-pressure calc-silicate rocks of the Münchberg gneiss complex, Bavaria, Germany. *J. Metamorph. Geol.* 12, 735–745.
- Liou, J.G., Kuniyoshi, S., Ito, K., 1974. Experimental studies of the phase relations between greenschist and amphibolite in a basaltic system. *Am. J. Sci.* 274, 613–632.
- Ludwig, K.R., 1994. ISOPLOT for MS-DOS, a plotting and regression program for radiogenic-isotope data, for IBM-PC compatible computers, version 2.75. Open-File Rep.-U.S. Geol. Surv. 191–445, October 11, 1994 revision.
- Mattinson, J.M., 1986. Geochronology of high-pressure–low-temperature Franciscan metabasites: a new approach using the U–Pb system. *Mem.-Geol. Soc. Am.* 164, 95–105.
- Meyer, C., Hemley, J.J., 1967. Wall rock alteration. In: Barnes, H.L. (Ed.), *Geochemistry of Hydrothermal Ore Deposits*. Holt, Reinhart and Winston, New York, pp. 135–166.
- Mezger, K., Rawnsley, C.M., Bohlen, S.R., 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.
- Mezger, K., Essene, E.J., van der Pluijm, B.A., Halliday, A.N., 1993. U–Pb geochronology of the Grenville Orogen of Ontario and New York: constraints on ancient crustal tectonics. *Contrib. Mineral. Petrol.* 114, 13–26.
- Miller, B.V., Dunning, G.R., Barr, S.M., Raeside, R.P., Jamieson, R.A., Reynolds, P.H., 1996. Magmatism and metamorphism in a Grenvillian fragment; U–Pb and $^{40}\text{Ar}/^{39}\text{Ar}$ ages from the Blair River Complex, northern Cape Breton Island, Nova Scotia, Canada. *Geol. Soc. Am. Bull.* 108, 127–140.
- Moecher, D.P., Anderson, E.D., Cook, C.A., Mezger, K., 1997. The petrogenesis of metamorphosed carbonatites in the Grenville Province, Ontario. *Can. J. Earth Sci.* 34, 1185–1201.
- Mortensen, J.K., Sontgomery, J.R., Fillipone, J., 1987. U–Pb zircon, monazite, and sphene ages for granitic orthogneiss of the Barkerville terrane, east-central British Columbia. *Can. J. Earth Sci.* 24, 1261–1266.
- Mortensen, J.K., Ciesielski, A., 1987. U–Pb zircon and sphene geochronology of Archean plutonic and orthogneissic rocks of the James Bay region and Bienville Domain, Quebec. *Pap.-Geol. Surv. Can.* 87-2, 129–134.
- Mortensen, J.K., 1993a. U–Pb geochemistry of the Lapparent

- Massif, northeastern Abitibi belt: basement or synvolcanic pluton? *Can. J. Earth Sci.* 30, 42–47.
- Mortensen, J.K., 1993b. U–Pb geochronology of the eastern Abitibi subprovince: Part 1. Chibougamau–Matagami–Joutel region. *Can. J. Earth Sci.* 30, 11–28.
- Mortensen, J.K., Card, K.D., 1993. U–Pb age constraints for the magmatic and tectonic evolution of the Pontiac Subprovince, Quebec. *Can. J. Earth Sci.* 30, 1970–1980.
- Motoyoshi, Y., Thost, D.E., Hansen, B.J., 1991. Reaction textures in calc-silicate granulites from the Bolingen Islands, Prydz Bay, East Antarctica: implications for the retrograde P–T path. *J. Metamorph. Geol.* 9, 293–300.
- Nemchin, A.A., Pidgeon, R.T., Wilde, S.A., 1994. Timing of Late Archean granulite facies metamorphism in the southwestern Yilgarn Craton of Western Australia: evidence from U–Pb ages of zircons from mafic granulites. *Precambrian Res.* 68, 307–321.
- Oberti, R., Smith, D.C., Rossi, G., Caucia, F., 1991. The crystal-chemistry of high-aluminum titanites. *Eur. J. Mineral.* 3, 777–792.
- Otsuki, M., Banno, S., 1990. Prograde and retrograde metamorphism of hematite-bearing basic schists in the Sanbagawa belt in central Shikoku. *J. Metamorph. Geol.* 8, 425–439.
- Patrick, B., 1995. High-pressure–low-temperature metamorphism of granitic orthogneiss in the Brooks Range, northern Alaska. *J. Metamorph. Geol.* 13, 111–124.
- Peacock, S.M., Norris, P.J., 1989. Metamorphic evolution of the Central Metamorphic Belt, Klamath Province, California: an inverted metamorphic gradient beneath the Trinity peridotite. *J. Metamorph. Geol.* 7, 191–209.
- Pidgeon, R.T., Bosch, D., Bruguier, O., 1996. Inherited zircon and titanite U–Pb systems in an Archean syenite from southwestern Australia: implications for U–Pb stability of titanite. *Earth Planetary Sci. Lett.* 141, 187–198.
- Resor, P.G., Chamberlain, K.R., Frost, C.D., Snoke, A.W., Frost, B.R., 1996. Direct dating of deformation; O–Pb age of Syndi-formational Sphere growth in the Proterozoic Laramic Peak Shear Zone. *Geology* 24, 623–626.
- Ribbe, P.H., 1980. Titanite. *Rev. Mineral.* 5, 137–154.
- Romer, R.L., Nisca, D.H., 1995. Svecofennian crustal deformation of the Baltic Shield and U–Pb age of late-kinematic tonalitic intrusions in the Burtrask shear zone, northern Sweden. *Precambrian Res.* 75, 1–2.
- Rötzler, J., Carswell, D.A., Gerstenberger, H., Haase, G., 1999. Transitional blueschist-epidote amphibolite facies metamorphism in the Frankenberg massif, Germany, and geotectonic implications. *J. Metamorph. Geol.* 17, 109–125.
- Schaltegger, U., Corfu, F., 1992. The age and source of large Hercynian magmatism in the central Alps: evidence from precise U–Pb ages and initial Hf isotopes. *Contrib. Mineral. Petrol.* 111, 329–344.
- Schaltegger, U., Schneider, J.-L., Maurin, J.-C., Corfu, F., 1996. Precise U–Pb chronometry of 345–350 Ma old magmatism related to syn-convergence extension in the Southern Vosges (Central Variscan Belt). *Earth Planetary Sci. Lett.* 144, 403–419.
- Schärer, U., Zhang, L.-S., Tapponnier, P., 1994. Duration of strike-slip movements in large shear zones: the Red River belt, China. *Earth Planetary Sci. Lett.* 126, 379–397.
- Schumacher, R., Schenk, V., Raase, P., Vitanage, P.W., 1990. Granulite facies metamorphism of metabasic and intermediate rocks in the Highland Series of Sri Lanka. In: Ashworth, J.R., Brown, M. (Eds.), *High-temperature Metamorphism and Crustal Anatexis*. Mineral. Soc. Ser. vol. 2, pp. 235–271.
- Scott, D.J., Machado, N., 1995. U–Pb geochronology of the northern Torngat Orogen, Labrador, Canada: a record of Paleoproterozoic magmatism and deformation. *Precambrian Res.* 70, 169–190.
- Scott, D.J., St-Onge, M.R., 1995. Constraints on Pb closure temperature in titanite based on rocks from the Ungava Orogen, Canada; implications for U–Pb geochronology and P–T–t path determinations. *Geology* 23, 1123–1126.
- Simonetti, A., Diog, R., 1990. U–Pb and Rb–Sr geochronology of Acadian plutonism in the Dunnage zone of the southeastern Quebec Appalachians. *Can. J. Earth Sci.* 27, 881–892.
- Smith, D.C., 1981. The pressure and temperature dependence of Al-solubility in sphene in the system Ti–Al–Ca–Si–O–F. *Prog. Exp. Petrol.*, Ser. D 18, 193–197.
- Spear, F.S., 1981. An experimental study of hornblende stability and compositional variability in amphibolite. *Am. J. Sci.* 281, 697–734.
- Stacey, J.S., Kramers, J.D., 1975. Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth Planetary Sci. Lett.* 26, 207–221.
- Studemeister, P.A., 1985. The greenschist metamorphism of Archean synvolcanic stocks near Wawa, Ontario, Canada. *J. Metamorph. Geol.* 3, 79–90.
- Taylor, M., Brown, G.E., 1976. High-temperature structural study of the $P2_1/a \rightleftharpoons A2/a$ phase transition in synthetic titanite CaTiSiO_5 . *Am. Mineral.* 61, 435–447.
- Terabayashi, M., 1993. Compositional evolution in Ca-amphibole in the Karmutsen metabasites, Vancouver Island, British Columbia, Canada. *J. Metamorph. Geol.* 11, 677–690.
- Thieblemont, D., Triboulet, C., Godard, G., 1988. Mineralogy, petrology and P–T–t path of Ca–Na amphibole assemblages, Saint-Martin des Noyers formation, Vendée, France. *J. Metamorph. Geol.* 6, 697–715.
- Timmermann, H., Parrish, R.R., Jamieson, R.A., Culshaw, N.G., 1997. Time of metamorphism beneath the Central Metasedimentary Belt boundary thrust zone, Grenville Orogen, Ontario: accretion at 1080 Ma? *Can. J. Earth Sci.* 34, 1023–1029.
- Tucker, R.D., Råheim, A., Krogh, T.E., Corfu, F., 1986. Uranium–lead zircon and titanite ages from the northern portion of the Western Gneiss Region, south-central Norway. *Earth Planetary Sci. Lett.* 81, 203–211.
- Tucker, R.D., Krogh, T.E., Råheim, A., 1990. Proterozoic evolution and age-province boundaries in the central part of the Western Gneiss Region, Norway: results of U–Pb dating of accessory minerals from Trondheimsfjord to Geiranger. *Geol. Assoc. Can. Spec. Pap.* 38, 149–173.
- Verts, L.A., Chamberlain, K.R., Frost, C.D., 1996. U–Pb sphene dating of metamorphism: the importance of sphene growth in the contact aureole of the Red Mountain Pluton, Laramie Mountains, Wyoming. *Contrib. Mineral. Petrol.* 125, 186–199.

- von Blackenburg, F., 1992. Combined high-precision chronometry and geochemical tracing using accessory minerals: applied to the Central-Alpine Bergell intrusion (central Europe). *Chem. Geol.* 100, 19–40.
- Wintsch, R.P., Aleinikoff, J.N., 1987. U–Pb isotopic and geologic evidence for Late Paleozoic anatexis, deformation, and accretion of Late Proterozoic Avalon Terrane, Southcentral Connecticut. *Am. J. Sci.* 287, 107–126.
- Wones, D.R., 1989. Significance of the assemblage titanite + magnetite + quartz in granitic rocks. *Am. Mineral.* 74, 744–749.
- Xirouchakis, D., Lindsley, D.H., 1998. Equilibria among titanite, hedenbergite, fayalite, quartz, ilmenite, and magnetite. Experiments and internally consistent thermodynamic data for titanite. *Am. Mineral.* 83, 712–725.
- Zalduegui, J.F.S., Schäfer, U., Ibarra, J.I.G., Girardeau, J., 1996. Origin and evolution of the Paleozoic Cabo Oretegal ultramafic–mafic complex (NW Spain): U–Pb, Rb–Sr and Pb–Pb isotope data. *Chem. Geol.* 129, 281–304.
- Zen, E.-A., 1974. Prehnite- and pumpellyite-bearing mineral assemblages, west side of the Appalachian metamorphic belt, Pennsylvania to Newfoundland. *J. Petrol.* 15, 197–242.
- Zhang, L.S., Schaerer, U., 1996. Inherited Pb components in magmatic titanite and their consequence for the interpretation of U–Pb ages. *Earth Planetary Sci. Lett.* 138, 1–4.
- Zheng, Y.-F., 1992. The three-dimensional U–Pb method: generalized models and implications for U–Pb two-stage systematics. *Chem. Geol.* 100, 3–18.
- Zweng, P.L., Mortensen, J.K., Dalrymple, G.B., 1993. Thermochronology of the Camflo gold deposit, Malartic, Quebec: implications for magmatic underplating and the formation of gold-bearing quartz veins. *Econ. Geol.* 88, 1700–1721.