

trillion yen in R&D in the five years 1996–2000, equivalent to \$74 billion in 1987 constant dollars. This represents a 35% increase over the amount spent in the previous five years. The slump has also led Japanese researchers to work harder than in the past to justify R&D spending and purchases of costly equipment. Now Japanese researchers are forced to be more conscious of efficiency and the bottom line. There is also an increase in collaborative R&D partnerships, be they within Japan or with international partners². During the period 1988–1993, almost 11% of Japan's scientific articles were internationally co-authored, up from 7% in the period 1981–1987 (ref. 1).

For a long time Japan was perceived to be a copycat good at adapting imported technology. Subsequently, Japan started beating the giants in their own strongholds – selling automobiles in the United States, watches in Switzerland, cameras in Germany, and consumer electronics in the entire world. Now Japanese companies receive more royalties and fees than they paid for technological know-how in several industry fields, including industrial chemicals, ceramics, iron and steel, and fabricated metals. In motor vehicles, the ratio of receipts to payments is 14 to 1. In 1994 Japan's export of advanced technology products of the United States was more than \$28 billion – twice the value of imports from the USA. Japan's trade surpluses come largely from computers, telecommunication and electronics and the deficits from aerospace and nuclear technology and software. The Japanese decision makers recognized that the

strategy of emphasizing research to adapt borrowed technology would not work in rapidly-developing technologies, such as biotechnology, gene therapy, and software for computer networks and that it was imperative to invest in fundamental science in a big way. As a consequence, industrial R&D spending in Japan which remained either stagnant or was declining every year since 1991 started increasing in the Japanese fiscal year 1995 (April 1995–March 1996). A survey of large Japanese companies has shown that the trend continued in fiscal year 1996 as well.

Japan is strong in technology and trade indicators. Not only has Japan the largest number of engineers as a proportion of its overall labour force among industrialized countries, but also the stock of scientists and engineers relative to labour force is increasing rapidly in Japan – at the rate of 8% annually during 1985–1990. It has more scientists and engineers engaged in R&D relative to its labour force (80 per 1,000 in 1993) than the USA (74 per 1,000). Despite its lead in technology and trade, Japan is still behind the US in R&D expenditures in higher education, in competitive research funding in universities, and in its share of the world's scientific articles. Japan is addressing these weaknesses by increasing the government science budgets for universities and national laboratories, and increasing national capacity for basic research and innovation¹.

A new Science and Technology Basic Law, passed in 1995, is a clear indication of Japan's seriousness in mobilizing basic research for recovery from recession. However, there was some

pruning of the budget for S&T in 1997 as part of the government-wide austerity effort. But the cuts affected mostly the expansion of some large-scale programmes such as nuclear energy and space research. Public spending on industrial technology-related R&D (e.g. programmes supported by the Ministry of International Trade and Industry) will experience some of the largest increases².

Japan will continue to be a major challenger, says Yoshida, in internationally competitive industries in the coming decade. It will be the world's second largest source of industrial R&D after the United States. Both the Japanese government and the Japanese companies view R&D as an important key to economic growth. During the eighties, the number of US patents granted to Japanese scientists and engineers increased at an average annual rate of 10.6% – from 7,000 in 1980 to 19,524 in 1990. In 1993, Japanese inventors received about 23% of all US patents – almost half of all patents granted to foreign inventors. That indeed is a measure of how strongly inventive the Japanese are.

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RESEARCH NEWS

Incorporation and diffusion of lead in zircons

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Zircon ($ZrSiO_4$) is among the most favoured minerals for age determination as it combines certain unique properties that make it suitable for this purpose. Once the mineral crystallizes, it is virtually stable for millions of years, retaining its crystallochemical characters,

resisting several of the chemical and physical breakdown processes in nature. Zircon occurs usually as an accessory mineral in several rocks and is carried as a detrital mineral, during weathering of its host rocks. Being quite refractory, it escapes remelting, except possibly

during extremely high grade granulite metamorphism. In its ability to incorporate appreciable amounts of radioactive elements like uranium and thorium during its crystallization (either as inclusions of uraninite, uranothorite and monazite or as substitutions for Zr^{4+} in

the crystal lattice) and also retain their decay products, zircon serves as a good radioactive clock. Further, a growing zircon crystal tends to reject entry of Pb owing to its size incompatibility ($\text{Pb}^{2+} = 1.29 \text{ \AA}$, $\text{Zr}^{4+} = 0.84 \text{ \AA}$) and hence all lead here is considered radiogenic, and, therefore, its accumulation within the zircon is a measure of its age. Also, the mineral's closure temperature (the temperature of the system at the time of zircon's determined age) being much above that of many granitic magmas, thermal resetting or alteration of the isotopic system does not take place. This is an additional property that makes the mineral useful, apart for geochronology, also for deciphering the origin and thermal history of igneous and metamorphic rocks. The oldest date – 4.3 billion years, recorded on detrital zircons from a sandstone, testifies to the mineral's survival, and its potential for geologic interpretation, inasmuch as this age-data have established the existence of still older zircon source rocks, thereby supporting the view of continental growth very early in the earth's history^{1,2}.

In spite of these positive features for geochronological applications, scientists do not have precise, quantitative information about (a) whether all the lead in zircons can indeed be wholly radiogenic, (b) whether common lead is totally excluded during the mineral's crystallization from melt or whether small amounts can still be incorporated in certain magmatic and metamorphic situations, and if so, can this non-radiogenic lead be distinguished from radiogenic lead for accurate age-dating, (c) do the radiogenic ^{206}Pb and other daughter products of U–Th, diffuse or become mobile when subject to prolonged periods of high thermal episodes, (d) what are their rates of diffusion, if any, and the consequent impact on age calculations. Geochronologists are aware of these problems in U–Th–Pb technique and many of the early pioneering workers have considered these aspects and determined zircon ages after incorporating appropriate steps in their calculations^{3,4}.

Recent experimental research carried out to quantify the extent of two major sources of discrepancy – incorporation of common lead and its diffusion, have provided some data to properly

evaluate these phenomena. In a work published early last year, E. B. Watson (Rensselaer Polytechnic Institute, New York) and colleagues have provided results of their experiments on incorporation of common lead within synthetically grown zircon⁵. Pb present in zircon is considered radiogenic since common or non-radiogenic lead (usually around 10–100 ppb) is geochemically incompatible in simple modes of geochemical substitution. Still, Pb has been reported (up to 612 ppm) from certain magmatic and metamorphic rocks under geochemically favourable situations^{6,7}. But how much of these non-radiogenic lead is present at substitutional lattice sites, or as mineral and fluid inclusions, is not known. In short, there is uncertainty about the mode of abundance of common lead in natural zircons. The experimental work of Watson and colleagues to study entry of Pb in synthetic crystals grown from Pb-rich silicate melts under igneous and hydrothermal settings is useful in this context. Though their results are in agreement with geochemically accepted incompatibility of Pb in zircon, they have shown that Pb^{2+} can still be substituted in lattice sites in both igneous and hydrothermal set ups, aided by favourable chemical environment, not considered rare in nature. In their experiments using igneous set up, they observed that presence of P^{5+} in the melt promoted incorporation of Pb^{2+} (as coupled substitution at Zr^{4+} sites), a feature to be taken note of in the case of zircons from granites, having an abundance of apatites. In the hydrothermal set up, they found incorporation of Pb^{2+} is more, and it also showed an inverse correlation with temperature. This inverse relationship, the authors feel, should be helpful in distinguishing zircons formed in wet environments in nature (hydrothermal and wet metamorphism) as they are likely to contain 'orders of magnitude more common lead than zircon grown under relatively dry conditions'. Here, unlike under igneous conditions, Pb^{2+} is able to enter zircon, even in the absence of P^{5+} , the charge balance here accomplished by incorporation of H^+ . Though these are only experimental observations, they are good qualitative indicators of behavioural tendencies of Pb in natural systems and hence its entry in zircon should not be considered as incompatible.

In the second contribution that appeared late last year, James Lee, Ian Watson and David Ellis (Australian National University, Canberra)⁸ have worked out diffusional aspects of radiogenic Pb in zircons. Quantitative data about this are not much known, though empirical models of diffusion kinetics have been worked out by earlier workers. This lack of data is essentially due to instrumental inadequacy to measure these elements, which are usually very low and often distributed heterogeneously in the small grains under study. A number of factors promote diffusion of elements, and particularly significant is the diffusion initiated by weakening of lattice by metamictization⁹ caused by bombardment of α -particles emitted during radioactive decay of U and Th within the mineral. This could result in unequal lattice expansion leading to fracturing¹⁰, though these damages to crystallinity of the grain are less pronounced in minerals having closely packed structure, or strong bond or high chemical stability like zircon¹¹. Yet, metamictization in zircon is not uncommon and under such a state, the mineral is liable for chemical leaching and alteration by fluids, and this is bound to lead to isotopic discordance. While such grains for dating purpose can be eliminated during preliminary selection, the need to know quantitatively the diffusion of U, Th and Pb, and their rates of mobility even in clear grains, however negligible, assume importance in view of their relevance to geochronological studies.

Lee and colleagues measured profiles of U, Th and Pb that have diffused out of well-crystallized natural zircon at natural concentrations instead of their profiles diffusing into synthetically grown crystals. They selected 572.1 m.y. old natural zircon from Sri Lanka, having low U (238 ppm), low Th (21 ppm) with relatively uniform U distribution and $^{238}\text{U}/^{206}\text{Pb}$ ratio (0.0928, $^{206}\text{Pb} = 19 \text{ ppm}$) showing excellent crystallinity. The analytical hurdles in estimation of low values of the elements were overcome by judicious use of a variety of techniques – scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), secondary ion mass spectrometry (SIMS), at appropriate stages of the experiment. Randomly

oriented, polished slices of this zircon were heated in platinum capsules with Specpure NaCl (the melt of which served as ion sink for diffusing cations) buffered with synthetic zircon powder and the mixtures were heated for 28–104 days at temperatures of 900°C (70–104 days), 1000°C (36–64 days) and 1100°C (28–51 days). At the end of the respective heating periods, the polished crystal surfaces were examined by SEM and they did not show any signs of reaction or dissolution. As anticipated, this thermal treatment had induced diffusion, and the near-surface Pb, U, Th gradient beneath the polished faces were measured to uniform depths using an ion probe (the penetration of the ions was confirmed to be uniform by atomic force microscopy). They found that Pb diffusion at 1100°C, was faster than those of U and Th by 4 orders of magnitude and between U and Th, that of U slightly faster. These are consistent with diffusivity model predicted, based on ionic radii of the cations ($U^{4+} = 1.00 \text{ \AA}$, $Th^{4+} = 1.05 \text{ \AA}$)⁸. According to them, the mobility of Pb is difficult to predict, in the absence of knowledge about the radius of the radiogenic Pb which, in turn, depends on its charge, which are 1.29 Å for Pb^{2+} , and 0.94 Å for Pb^{4+} . They, therefore, based their calculations using volume diffusion functions, and have concluded that in zircon 'Pb diffusional anisotropy is not significant'.

In the opinion of Lee *et al.*, diffusion coefficients for U and Th at 1100°C are so very low ($\sim 10^{-20} \text{ cm s}^{-1}$) that they are considered unlikely to diffuse out under most geological conditions and hence the 'closure temperature of Pb–U–Th isotopic system in zircon is determined by the diffusion rate of Pb', which according to their experiments for a 'zircon 200 µm diameter which has cooled at rates of 1, 5 and 10°C Myr⁻¹ are 899 ± 7, 926 ± 6 and 938 ± 5°C respectively'. These indicate maximum values for 'radiation damaged zircon' (since α-particles cause defects that may enhance diffusion rates) and minimum values for similar zircons 'annealed at modest temperature (200–700°C) over geological time scales'⁸. Extrapolating in terms of geological periods, their diffusion coefficients yield a mean Pb migration distance of ~0.5 cm at 1100°C after 45 myr, 'implying that even large (1 cm) mantle zircon could

lose most of their radiogenic Pb after this duration of heating', and if negligible radiogenic lead loss is reported, for example in mantle formed old zircons, it means that the crystal must have been transported to cooler levels in lower crust, subsequent to crystallization⁸.

Needless to point out, the incorporation of Pb in zircon during its growth from melt and its diffusion later over geologic time, unless properly recognized, pose risk of overestimation and underestimation of ages by the U–Pb technique. The experiments performed by Watson *et al.* and Lee *et al.* clearly point to the need to precisely know the quantum of common lead at the substitutional sites and their diffusional kinetics over geologic period under varying thermal regimes. The work of Watson and others point to the fact that entry of Pb^{4+} at Zr^{4+} sites rarely takes place in nature owing to lack of sufficient oxidizing conditions that can stabilize Pb^{4+} ; and also, Pb^{2+} is not as incompatible as assumed, a point pertinent to geochronological assumptions about Pb in zircons. These call for efforts to distinguish the incorporated non-radiogenic Pb. They also emphasize that one cannot assume that radiogenic Pb atoms may be tetravalent, on size basis, since they are decay products of U^{4+} or Th^{4+} . Such an assumption based on tetravalent parentage is not supported by the physics of the decay process which involves a number of intermediate products before Pb atoms are finally yielded. It is possible, on the other hand, that radiogenic lead atoms assume the same valence as common lead (Pb^{2+}) incorporated while zircon crystallized in which case the two are indistinguishable. Another aspect of the diffusional kinetics of Pb that has been highlighted by Watson *et al.* is that accumulation of radiogenic lead steadily builds up a chemical potential within the zircon as it ages, and this enhances diffusive Pb loss. They point out that if most of the radiogenic Pb have indeed diffused into zircon lattice sites, their exit from the crystal through diffusion is difficult without charge compensation, because Pb^{2+} only partially compensates the imbalance created by the decay of 4⁺ ions. However, this deficiency is thought to be overcome by influx of H (hydrous environment) which would stabilize radiogenic lead that accumu-

lates and prevent rise of chemical potential leading to Pb loss, a process analogous to influx of Pb^{2+} into zircon when H^+ is available for charge compensation. Hence Pb loss could occur only by exchange of radiogenic Pb with common lead or other cations⁵.

Zircons are known to grow under varying geologic temperature ranges – igneous, hydrothermal, metamorphic and sedimentary. The data from the two experiments, on incorporation and on diffusion, point to the need for scrupulous evaluation, for possible isotopic discordance. Particularly called for is an assessment of the geological pre-history of the mineral, right from its initial growth to subsequent thermal and other de-stabilizing geological events inevitable for a mineral like zircon having a high survival potential for millions of years and recognition of possible incorporation of (a) Pb^{4+} at Zr^{4+} sites under certain geological conditions and (b) that of Pb^{2+} in melts rich in P and/or H_2O (hydrothermal and wet metamorphic environments), and (c) discrimination of non-radiogenic and radiogenic varieties, as well those from inclusions (fluid-, glass-, or mineral).

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