

Seawater intrusion through the oceanic crust and carbonate sediment in the Equatorial Pacific: Lithium abundance and isotopic evidence

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[1] Large-scale lateral advection of seawater within the oceanic crust is thought to be the cause of low heat flow in the Equatorial Pacific. Until now supportive evidence is limited to reversals of B and $\delta^{11}\text{B}$, Ca, Mg, SO_4^{2-} , Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ in sediment pore waters. Here we report new evidence from a detailed study of Li and its isotopes in sediment cores from ODP Sites 844 and 851. Carbonates at these sites were significantly recrystallized leading to large variations in Li and $\delta^7\text{Li}$ in the sediments and associated pore waters. In addition to diagenetic effects, distinct reversals in lithium concentration and isotopic ratio toward modern seawater composition are observed in waters near the basaltic basement, lending further support to the seawater intrusion hypothesis. Three endmembers are identified in the pore waters: seawater, a diagenetically altered component, and evolved crustal fluid. The new lithium isotopic results underscore the importance of diagenetic artifacts in carbonate sediments. **INDEX TERMS:** 1040 Geochemistry: Isotopic composition/chemistry; 1045 Geochemistry: Low-temperature geochemistry; 1050 Geochemistry: Marine geochemistry (4835, 4850); 3015 Marine Geology and Geophysics: Heat flow (benthic) and hydrothermal processes; **KEYWORDS:** Li isotopes, carbonate, pore waters, diagenesis. **Citation:** You, C.-F., L.-H. Chan, J. M. Gieskes, and G. P. Klinkhammer, Seawater intrusion through the oceanic crust and carbonate sediment in the Equatorial Pacific: Lithium abundance and isotopic evidence, *Geophys. Res. Lett.*, 30(21), 2120, doi:10.1029/2003GL018412, 2003.

1. Introduction

[2] Heat fluxes associated with seawater circulation on the mid-ocean ridges provide crucial insights into the global heat balance in the oceanic crust [McKenzie, 1967; Langseth et al., 1965; Sclater et al., 1976]. Several geophysical models have indicated that the off-axis heat flow may be far more significant than the high temperature axial flow [Elderfield and Schultz, 1996; Schultz et al., 1992]. In the eastern Equatorial Pacific, it has long been recognized that surface conductive heat flow is significantly lower than theoretically predicted [Langseth et al., 1965; Sclater et al., 1980]. Recent geochemical studies in pore waters have

concluded that large quantities of seawater may have intruded below thick sediments thereby accounting for the anomalously low heat flow in this area [Baker et al., 1991; Oyun et al., 1995; Spivack and You, 1997]. The chemical compositions of the deepest pore waters are similar to the present-day seawater in Ca, Mg, SO_4^{2-} , Sr and $^{87}\text{Sr}/^{86}\text{Sr}$, suggestive of a short water residence time and minimum water-rock interaction within the basement. Based on B and $\delta^{11}\text{B}$ results at Ocean Drilling Program (ODP) Site 851B, a replacement time of 3600 years for the advecting fluids has been estimated [Spivack and You, 1997]. Seawater intrusion in permeable basement rocks below a thick sediment cover has also been documented on the Juan de Fuca Ridge [Wheat and Mottl, 2000].

[3] Lithium isotopic composition has been used as a diagnostic tracer in marine geochemistry. In particular, the large isotopic fractionation at low to moderate temperatures is suitable for studying water-rock and water-sediment interactions [e.g., Chan et al., 1992, 1993, 1994; Zhang et al., 1998; Chan and Kastner, 2000]. Li in marine carbonates is a potentially important indicator of seawater composition of the past but the chemical and isotopic records may be masked by diagenetic effects [Hoefs and Sywall, 1997; Kosler et al., 2001]. In this study, we measured the down-core distributions of Li and $\delta^7\text{Li}$ in carbonate sediments and associated pore waters in the eastern equatorial Pacific. This permits a detailed examination of the diagenetic processes in carbonate-rich sediments with further assessment of the seawater intrusion hypothesis.

2. Samples and Analytical Methods

[4] Ocean Drilling Program (ODP) Holes 851B and 844B were drilled during Leg 138 in the Guatemala basin and the Eastern Equatorial Pacific respectively [Meyer et al., 1992]. The sediments are dominantly nannofossil and foraminifer oozes with interspersed radiolarians and diatoms. In Hole 851B substantial amounts of clay are distributed at depths 150 to 180 meters below seafloor (mbsf). A layer of metalliferous sediments at 317 m is indicative of hydrothermal activity approximately 9 Ma ago [Gurvich et al., 1995]. Pore waters were extracted using a stainless steel squeezer. Bulk sediments were dried, pulverized and sonicated in sub-boiling water before dissolving the carbonate fraction in dilute acetic acid. Li concentrations in carbonates and pore waters were determined by isotope dilution and flame emission. Li separation for isotope analysis followed procedures described in You and Chan [1996]. Li isotopic ratios were determined by thermal ionization mass spectrometry, using Li_3PO_4 as an ion source. The precision is better than $\pm 1\%$ (1σ). Li

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isotopic composition is expressed as $\delta^7\text{Li}$ relative to NIST standard L-SVEC.

3. Results and Discussion

[5] Large down-core Li and $\delta^7\text{Li}$ variations occur in the pore waters (Figure 1). At Site 851B, Li decreases from a seawater value near the sediment/water interface to a distinct minimum of $9.6\ \mu\text{M}$ at 200 mbsf and returns to the seawater value near the basement. $\delta^7\text{Li}$ increases from a seawater value at surface to a maximum value of 56.3‰ at 200 m and then decreases to 18.8‰ near the basement at Site 851B. Li and $\delta^7\text{Li}$ variations at Site 844B are less pronounced, but the reversals remain unambiguous. Li concentrations in the carbonates at Site 851B vary between 0.3 and 1.0 ppm, with the exception of the metalliferous sediments at 317 m, which has 10 ppm Li (Figure 2). $\delta^7\text{Li}$ increases from 6.2‰ at the core top to a maximum of 32.0‰ at 200 m and then decreases down-core to 8.1‰ .

[6] The Li and $\delta^7\text{Li}$ reversals in pore waters at Sites 844B and 851B support strongly previous suggestions of lateral advection of seawater within the permeable oceanic crust in the Equatorial Pacific [Baker *et al.*, 1991]. The Li concentration in the near basement water is identical to present-day seawater, but the shifted Li isotopic composition implies that other reactions are involved. The down-core decrease in pore water Li is a result of diagenesis and the higher $\delta^7\text{Li}$

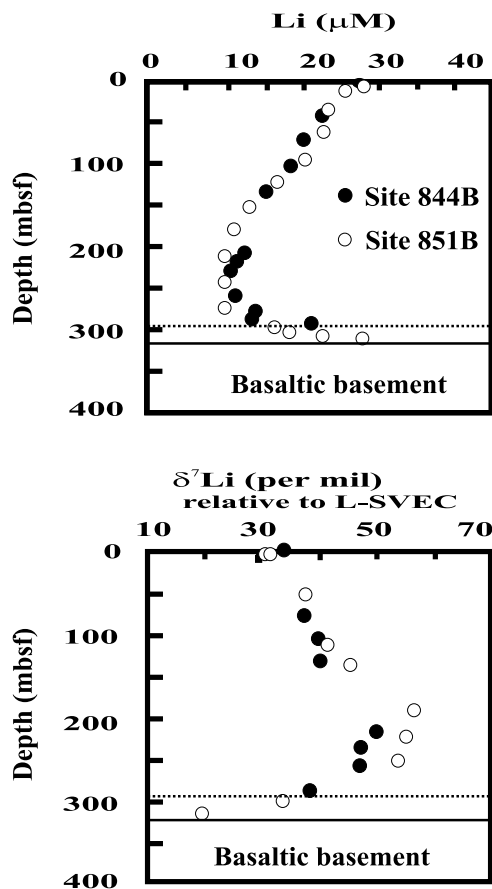


Figure 1. The down-core distributions of Li and $\delta^7\text{Li}$ in pore waters of ODP Sites 844B (filled circles) and 851B (open circles).

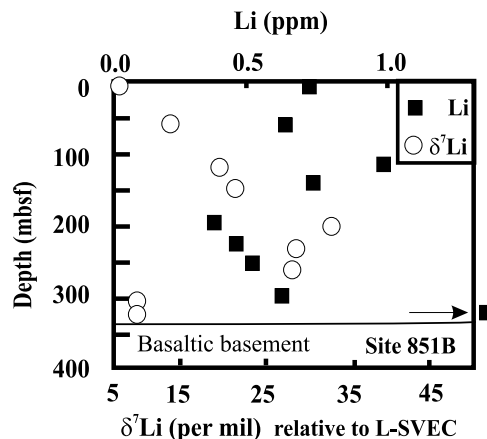


Figure 2. The down-core distributions of Li (filled squares) and $\delta^7\text{Li}$ (open circles) in carbonates of ODP Sites 851B.

values suggest that ^6Li has been preferentially removed. Pore water Sr concentrations [Oyun *et al.*, 1995] show an interesting anti-correlation with Li. Recrystallization of Sr-rich biogenic calcite results in an increase of Sr content in pore waters. The inverse relation with Sr indicates that Li is removed from pore water during carbonate recrystallization. However, the most Li-poor carbonates were found at the zone of maximum diagenesis (Figure 2). This argues against carbonates as the major sink, but instead implies that Li is taken up by clays.

[7] The carbonates at 851B show a similar Li concentration range as reported for foraminiferal calcite. Biogenic carbonates contain 0.5 to 2.6 ppm Li possibly regulated by temporal variation in ocean chemistry and/or diagenetic processes after burial [Hoefs and Sywall, 1997; Delaney *et al.*, 1985]. Li variations in carbonates associated with changing hydrothermal input have been proposed [Delaney and Boyle, 1984; Hoefs and Sywall, 1997]; however, there was no evaluation of the diagenetic effects. The unusually high Li content in carbonates at 317 m coincides with the presence of Fe-Mn oxide sediments, which are most likely of hydrothermal origin [Gurvich *et al.*, 1995]. This is consistent with elevated Li concentrations in hydrothermal fluids from ocean spreading centers [Chan *et al.*, 1993, 1994].

[8] Holocene foraminiferal shells display an average $\delta^7\text{Li}$ of 19‰ compared with a much larger range of 2 to 43.8‰ in the Tertiary [You and Chan, 1996; Hoefs and Sywall, 1997]. Since Li has an oceanic residence time of at least 400,000 years, large short-term variation in $\delta^7\text{Li}$ is not expected. Hoefs and Sywall [1997] proposed a non-steady state model with time-dependent hydrothermal inputs to explain the $\delta^7\text{Li}$ variations in planktonic foraminifera in the Quaternary and Tertiary. This requires an increase in the hydrothermal flux up to a factor of two or a decrease in fluvial input to half to produce a possible 15‰ $\delta^7\text{Li}$ shift in seawater. The new Li isotopic results obtained here, however, underscore the importance of diagenetic artifacts. The carbonates in Site 851B exhibit an isotopic range (6 to 32‰) similar to the above mentioned range. Another striking feature is that the down-core variation in the carbonate phase parallels that of the associated pore waters.

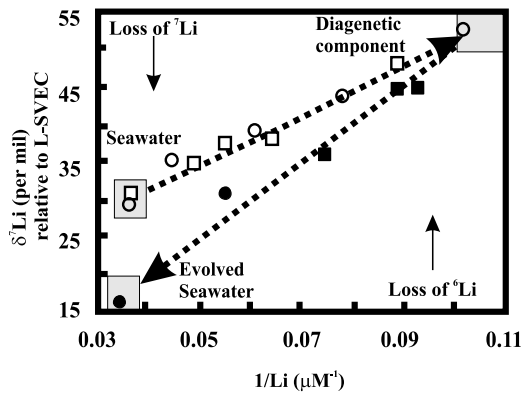


Figure 3. The $\delta^7\text{Li}$ versus $1/\text{Li}$ plot in pore waters of ODP Sites 844B (filled circles, >250 m; open circles, <250 m) and 851B (filled squares, >250 m; open squares, <250 m).

The co-variation of $\delta^7\text{Li}$ between the carbonates and the associated pore waters indicates water-sediment interactions during diagenesis, rather than temporal variation in oceanic source and sinks. This notion is supported by identification of diagenetically altered carbonates within the lower part of the sedimentary column. Similar changes on B and $\delta^{11}\text{B}$ in carbonates have been documented at Site 851 [Spivack and You, 1997], as well as in corals [Gaillardet and Allegre, 1995]. Assuming isotopic equilibrium is reached, the mineral-water fractionation factor (α) is estimated to be 0.976 ± 0.001 . In contrast, recent measurements show a small Li isotopic fractionation in foraminiferal shells [Kosler et al., 2001]. This difference emphasizes potential diagenetic artifacts in carbonate sediments and needs further investigation.

[9] Pore water data in both holes yield two linear mixing trends as a function of depth in the plot of $\delta^7\text{Li}$ versus $1/\text{Li}$ (Figure 3). Three distinct Li reservoirs are identified down core: seawater, a diagenetic component, and evolved crustal fluid. The two trends converge at 250 m where the zone of maximum diagenesis is located. The pore waters at shallow depths maintain seawater-like compositions. In strong contrast, the diagenetic component has a much higher $\delta^7\text{Li}$ and lower Li (56‰ and $10 \mu\text{M}$ respectively). This $\delta^7\text{Li}$ represents the heaviest Li isotopic composition in fluids ever reported and indicates an extreme loss of ^6Li during diagenesis. The composition in basement fluid can be inferred from the deepest pore water. The deepest pore water has a Li concentration identical to that of present-day seawater. Similar seawater-like concentrations have been reported for other elements [Baker et al., 1991; Oyun et al., 1995]. However, the shift of $\delta^7\text{Li}$ from a seawater value (32.4‰) [You and Chan, 1996] to 18.8‰ in this water implies that interactions with the oceanic crust have occurred. Three different type of carbonates can be discerned from the $\delta^7\text{Li}$ versus $1/\text{Li}$ plot, namely biogenic (6–12‰), diagenetic (32‰) and hydrothermally altered (8‰) (Figure 4). Unlike the porewaters, however, the carbonates do not display simple mixing relationships among the three components. This may in part reflect natural variations of Li and $\delta^7\text{Li}$ in biogenic calcites formed at different times [Hoefs and Sywall, 1997]. On the other hand, the deeper carbonates show lighter isotopic compositions relative to younger samples. The two deepest samples

have extremely low isotopic compositions (8‰), probably related to previous hydrothermal activity. It appears that the Li isotope ratio can be a sensitive diagnostic tool for evaluation of diagenetic artifacts in carbonates.

[10] The evolved crustal fluid has a lighter $\delta^7\text{Li}$ (18.8‰), but retains the seawater concentration. This shift in $\delta^7\text{Li}$ is due to either isotopic exchange with the hydrothermally altered carbonates or an imprint of seawater-basalt interaction during seawater circulation. If the later case were true, the reaction temperature can be estimated from the empirical Li isotope fractionation during seawater alteration of oceanic crust. The deepest pore water shows an isotopic fractionation factor of 0.985 relative to fresh basalt, equivalent to temperature of $\sim 80^\circ\text{C}$ based on the study of ocean crust alteration at ODP site 504B [Chan et al., 2002]. This estimated temperature is too low to mobilize Li from basalt. Experiments have shown that Li is released only when temperature reaches above 150°C but is taken up by basalt at lower temperatures with preferential incorporation of ^6Li [Chan et al., 1994; Seyfried et al., 1984]. Secondly, the derived temperature would be sufficient for altering significantly the concentrations of Ca, Mg, SO_4^{2-} , Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ in the crustal fluids, which is contrary to observations of the near-basement waters. Isotopic exchange after burial between pore waters and the altered carbonates offers an alternative explanation. In other words, the water emerging from the basement has a similar composition as the present-day seawater and subsequent exchange with the hydrothermally altered sediment has caused a shift of $\delta^7\text{Li}$ toward lighter values.

[11] We can estimate the water residence time in the same area based on the Li profile of ODP 851 using the approach of Baker et al. [1991]. Using the concentration gradient of the lowest 24 m section, an average porosity of 72% [Meyer et al., 1992], and diffusion coefficient of $1.48 \times 10^2 \text{ cm}^2/\text{yr}$ [Li and Gregory, 1974], the diffusive flux of Li from the basement is $0.41 \text{ nmol}/\text{cm}^2/\text{yr}$. Assuming a 200 m permeable zone with 20% porosity in the basement [Baker et al., 1991], Li in the basement water should decrease at a rate of $1 \times 10^{-10} \text{ mol}/\text{L}$ per year. A measurable decrease in $1 \mu\text{M}$ would require 10,000 years. Since the basal pore water has

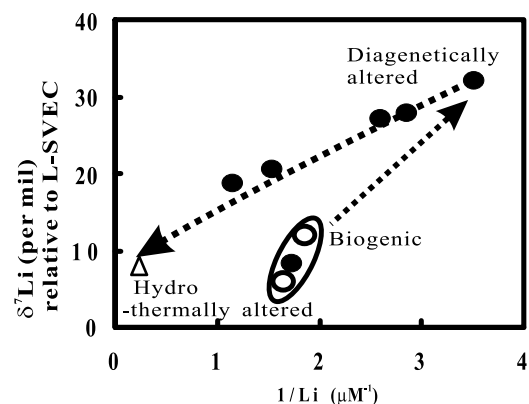


Figure 4. The $\delta^7\text{Li}$ versus $1/\text{Li}$ plot in carbonates of ODP Site 851B. Carbonates at depth between 100 and 260 m fall on a mixing trend between a diagenetic and a hydrothermally altered component. Symbols: filled circles, 100–260 m; open circles, >60 m; open triangles, >260 m.

the same Li content as seawater, the age of the basement must be younger than 10,000 years. This is consistent with the maximum residence time of 12,000 years based on Sr isotope data [Baker et al., 1991] and the water replacement time of 3600 years estimated from the B data [Spivack and You, 1997].

4. Conclusions

[12] The reversals of Li and $\delta^7\text{Li}$ in pore waters near the basement toward seawater composition provide strong support for large-scale seawater intrusion through the upper part of oceanic crust. This work confirms previous observations of sea water intrusion in the Eastern Equatorial Pacific, a process that is responsible for the low-conductive heat flow in the area. Base on the Li data, we estimate that the maximum age of the water residence time in the basement to be 10,000 years. At the same time, we have documented for the first time the effects of diagenesis and hydrothermal alteration on the distribution of Li and $\delta^7\text{Li}$ in carbonate sediments. This information is crucial for future applications of Li/Ca and Li isotope records of marine carbonates for paleoceanographic studies.

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References

- Baker, P. A., P. M. Stout, M. Kastner, and H. Elderfield, Large-scale lateral advection of seawater through ocean crust in the Central Equatorial Pacific, *Earth Planet. Sci. Lett.*, *105*, 522–533, 1991.
- Chan, L. H., J. M. Edmond, G. Thompson, and K. Gillis, Lithium isotopic composition of submarine basalts: Implications for the lithium cycle in the oceans, *Earth Planet. Sci. Lett.*, *108*, 151–160, 1992.
- Chan, L. H., J. M. Edmond, and G. Thompson, A lithium isotope study of hot springs and metabasalts from mid-ocean ridge hydrothermal systems, *J. Geophys. Res.*, *98*, 9653–9659, 1993.
- Chan, L. H., J. M. Gieskes, C. F. You, and J. M. Edmond, Lithium isotope geochemistry of sediments and hydrothermal fluids of the Guaymas Basin, Gulf of California, *Geochim. Cosmochim. Acta*, *58*, 4443–4454, 1994.
- Chan, L. H., and M. Kastner, Lithium isotopic compositions of pore fluids and sediments in the Costa Rica subduction zone: Implications for fluid processes and sediment contribution to the arc volcanoes, *Earth Planet. Sci. Lett.*, *183*, 275–290, 2000.
- Chan, L. H., J. C. Alt, and D. A. H. Teagle, Lithium and lithium isotope profiles through the upper oceanic crust: A study of seawater-basalt exchange at ODP Sites 504B and 896A, *Earth Planet. Sci. Lett.*, *2001*, 187–201, 2002.
- Delaney, M. L., and E. A. Boyle, Lithium in foraminiferal shells: Implications for high-temperature hydrothermal circulation fluxes and oceanic crustal generation rates, *Earth Planet. Sci. Lett.*, *80*, 91–105, 1984.
- Delaney, M. L., A. W. Be, and E. A. Boyle, Li, Sr, Mg, and Na in foraminiferal calcite shells from laboratory culture, sediment traps and sediment cores, *Geochim. Cosmochim. Acta*, *49*, 1327–1341, 1985.
- Elderfield, H., and A. Schultz, Mid-ocean ridge hydrothermal fluxes and the chemical composition of the ocean, *Annu. Rev. Earth Planet. Sci. Lett.*, *24*, 191–224, 1996.
- Gaillardet, J., and C. J. Allegre, Boron isotopic compositions of corals: Seawater or diagenesis record?, *Earth Planet. Sci. Lett.*, *136*, 665–676, 1995.
- Gurvich, E. G., M. A. Levitan, and T. G. Kuzmina, Chemical composition of Leg 138 sediments and history of hydrothermal activity, in *Proc. Ocean Drill. Program Sci. Res.*, edited by N. G. Pisias et al., (Ocean Drilling Program, College Station, TX, 1995), *138*, 769–778, 1995.
- Hoefs, J., and M. A. Sywall, Lithium isotope composition of Quaternary and Tertiary biogenic carbonates and a global lithium isotope balance, *Geochim. Cosmochim. Acta*, *61*, 2679–2690, 1997.
- Kosler, J., M. Kucera, and P. Sylvester, Precise measurement of Li isotopes in planktonic foraminiferal tests by quadrupole ICPMS, *Chem. Geol.*, *181*, 169–179, 2001.
- Langseth, M. G., P. J. Grim, and M. Ewing, Heat flow measurements in the East Pacific Ocean, *J. Geophys. Res.*, *70*, 367–380, 1965.
- Li, Y. H., and S. Gregory, Diffusion of ions in seawater and in deep sea sediments, *Geochim. Cosmochim. Acta*, *38*, 703–714, 1974.
- McKenzie, D. P., Some remarks on heat flow and gravity anomalies, *J. Geophys. Res.*, *72*, 6261–6273, 1967.
- Meyer, L., N. Pisias, T. Janecek, et al., *Proc. Ocean Drill. Program*, Init. Repts. 138, College Station, TX (Ocean Drilling Program), 1992.
- Oyun, S., H. Elderfield, and G. P. Klinkhammer, Strontium isotopes in porewaters of east equatorial Pacific sediments from Leg 138: Indicators of seawater advection through oceanic crust and sediments, in *Proc. Ocean Drill. Program Sci. Res.*, edited by N. G. Pisias et al., (Ocean Drilling Program, College Station, TX), *138*, 813–819, 1995.
- Schultz, A., J. R. Delaney, and R. E. McDuff, On the partitioning of heat flux between diffuse and point source seafloor venting, *J. Geophys. Res.*, *97*, 12,299–12,314, 1992.
- Slater, J. G., J. R. Crowe, and N. Anderson, On the reliability of oceanic heat flow average, *J. Geophys. Res.*, *81*, 2997–3006, 1976.
- Slater, J. G., C. Jaupart, and D. Galson, The heat flow through oceanic and continental crust and the heat loss of the Earth, *Rev. Geophys.*, *18*, 269–311, 1980.
- Seyfried, W. E., D. R. Janecky, and M. Mottl, Alteration of oceanic crust: Implications for geochemical cycles of lithium and boron, *Geochim. Cosmochim. Acta*, *48*, 557, 1984.
- Spivack, A. J., and C. F. You, Boron isotopic geochemistry of carbonates and pore waters, Ocean Drilling program Site 851, *Earth Planet. Sci. Lett.*, *152*, 113–122, 1997.
- Wheat, C. G., and M. J. Mottl, Composition of pore water and spring waters from Baby Bare: Global implications of geochemical fluxes from a ridge flank hydrothermal system, *Geochim. Cosmochim. Acta*, *64*, 629–642, 2000.
- You, C. F., and L. H. Chan, Precise determination of lithium isotopic composition in low concentration natural samples, *Geochim. Cosmochim. Acta*, *60*, 909–915, 1996.
- Zhang, L., L. H. Chan, and J. M. Gieskes, Lithium isotope geochemistry of pore waters from Ocean Drilling Program Sites 918/919, Irminger Basin, *Geochim. Cosmochim. Acta*, *62*, 2437–2450, 1998.

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