Titanium in Quartz: A Case Study of Sediment Provenance, South Island, New Zealand*

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Abstract

Quartz is an essential constituent of siliciclastic sediment that has a wide variety of potential primary and recycled sources. Recent experimental calibrations have shown that titanium (Ti) substitution into quartz is proportional to temperature, pressure, and TiO_2. We have explored the use of Ti and other trace elements in detrital quartz as a “fingerprint” of sediment provenance in modern rivers and ancient basins of the South Island of New Zealand. Measurements of low levels of Ti and other trace elements in quartz are done routinely by LA-ICP-MS on grain separates and polished thin sections. Raw intensity data are normalized via analyses of the NIST 610 glass standard to obtain trace element concentrations.

Detrital quartz in Permian-Jurassic greywacke sandstones exhibit uniformly high Ti concentrations that reflect plutonic sources. Regional metamorphism of these rocks has resulted in heterogeneous re-equilibration at lowest grade and systematic increases in quartz Ti concentrations that accompany recrystallization from medium- to high-grade. The latter provide metamorphic P-T estimates that agree with previous thermobarometry.

Quartz in bedload sediment from modern rivers that drain these metasedimentary rocks in the Southern Alps has Ti concentrations that correlate with metamorphic grade of upstream bedrock. Some samples exhibit smooth variation of quartz Ti concentrations with grain size that indicate hydrodynamic fractionation of sediment from heterogeneous sources.

Titanium concentrations in detrital quartz from Cretaceous-Neogene siliciclastic deposits exhibit distinct shifts with age and location. Cretaceous sandstones and conglomerates contain quartz with Ti concentrations that are consistent with derivation from local igneous and metamorphic bedrock. Paleogene sandstones have quartz with higher Ti concentrations that require derivation from distal granitic or greywacke sources during marine transgression. Neogene samples contain quartz with a bimodal distribution of quartz having high and low Ti concentrations that probably reflect reworking of underlying deposits during marine regression.

Taken together, these results demonstrate Ti-in-quartz to be a powerful tool in accessing the provenance of siliciclastic sediment.

References

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Thomas, J.B.,E.B. Watson, F.S. Spear, P.T. Shemella, S.K. Nayak, and A. Lanzirotti, 2010, TitaniQ under pressure: the effect of pressure and temperature on the solubility of Ti in quartz: Contributions to Mineralogy and Petrology, Springer, v. 160, 743-759.

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Titanium in Quartz

A Case Study of Sediment Provenance, South Island, New Zealand

Candace E. Martin & J. Michael Palin

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Lots of detrital quartz, but where did it come from?

Titanium (Ti^{4+}) Substitutes for Silicon (Si^{4+}) in Quartz

$$(1\text{-}x)\ SiO_2 \quad + \quad x\ TiO_2 \quad = \quad (Si,Ti)O_2$$

lo-T quartz — rutile — hi-T quartz

Presenter's notes: Recent experimental calibrations have shown that titanium (Ti) substitution into quartz is proportional to temperature, pressure, and TiO_2.

Titanium (Ti^{4+}) Substitutes for Silicon (Si^{4+}) in Quartz

$$(1-x)\ SiO_2 \quad + \quad x\ TiO_2 \quad = \quad (Si,Ti)O_2$$

lo-T quartz — rutile — hi-T quartz

Thomas et al. (2010, CMP) experimentally-based calibration:

$$T(^{\circ}\mathrm{C}) = \frac{a + cP}{b - R \times \ln X_{\mathrm{TiO_2}}^{\mathrm{Qtz}} + R \times \ln a_{\mathrm{TiO_2}}} - 273.15$$

Titanium (Ti^{4+}) Substitutes for Silicon (Si^{4+}) in Quartz

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lo-T quartz   rutile   hi-T quartz

Thomas et al. (2010, CMP) experimentally-based calibration:

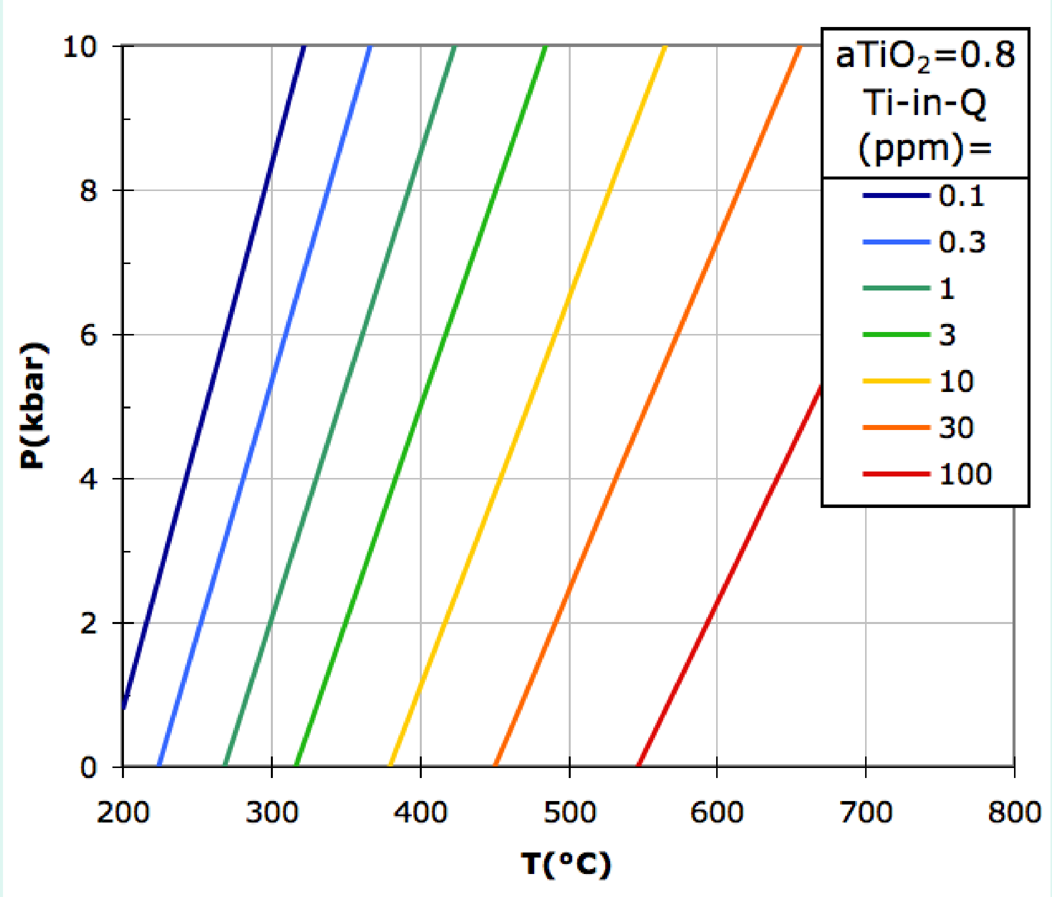
$$T(^\circ C) = \frac{a + cP}{b - R \times \ln X_{TiO_2}^{Qtz} + R \times \ln a_{TiO_2}} - 273.15$$

calculated Ti-in-quartz temperatures are:

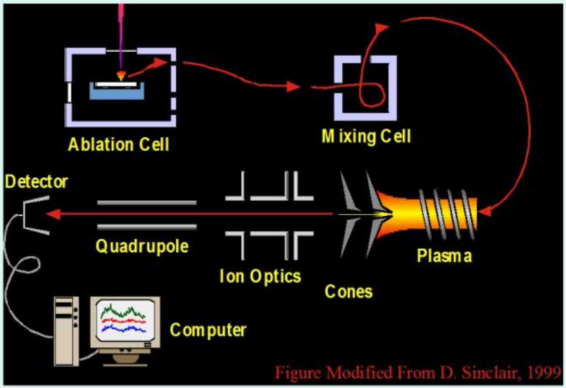
+ve functions of [Ti] & est'd P

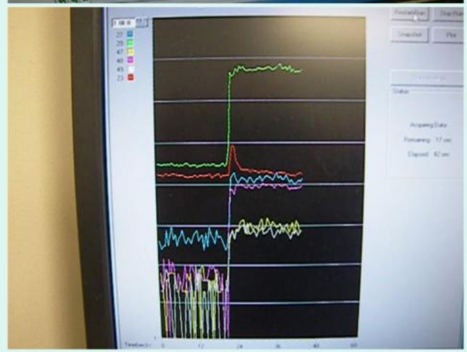
-ve functions of est'd $a(TiO_2)$

NOTE: alternative calibration of Huang & Audetat (2012, GCA)



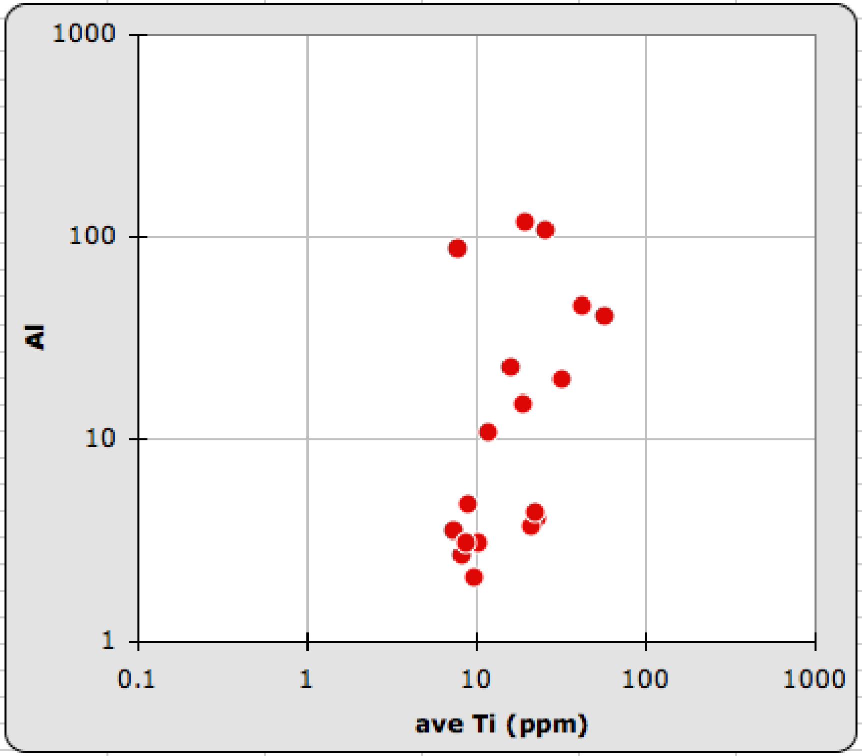
Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

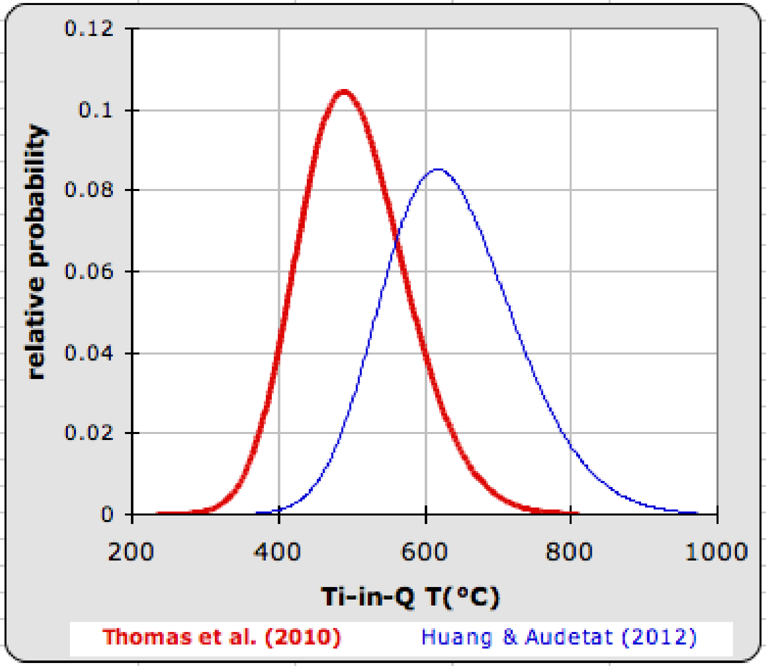




Presenter's notes: Measurements of low levels of Ti and other trace elements in quartz are done routinely by LA-ICP-MS on grain separates and polished thin sections. Raw intensity data are normalized via analyses of the NIST 610 glass standard to obtain trace element concentrations.

Ion Count Rates > Concentrations > Temperatures



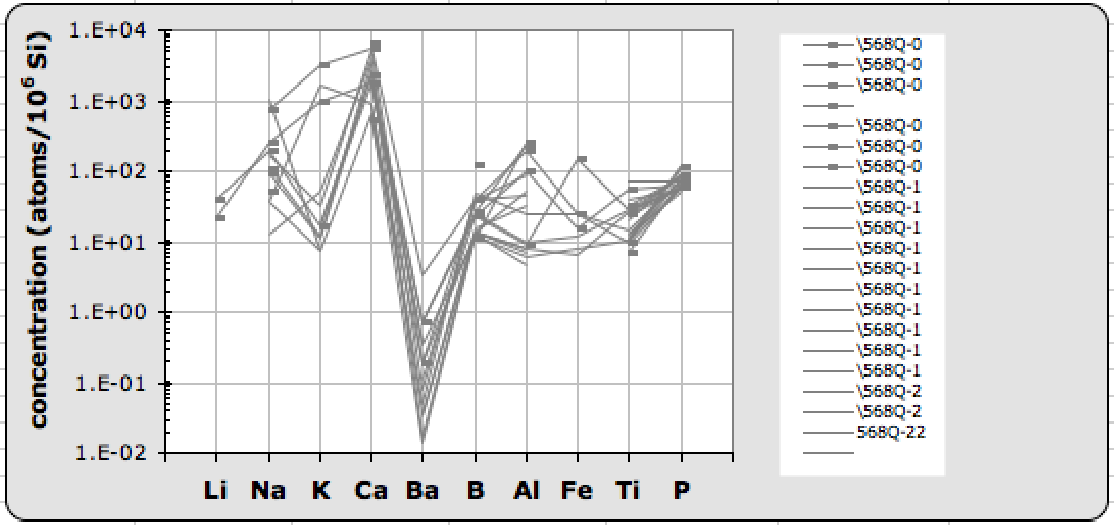


P68568

T(T10)°C	± (1 se)
497	**13**
T(HA12)°C	± (1 se)
628	**16**
n= 19 of 19	
$a(TiO_2)$	
0.8	**0.2**
P(kbar)	
5	

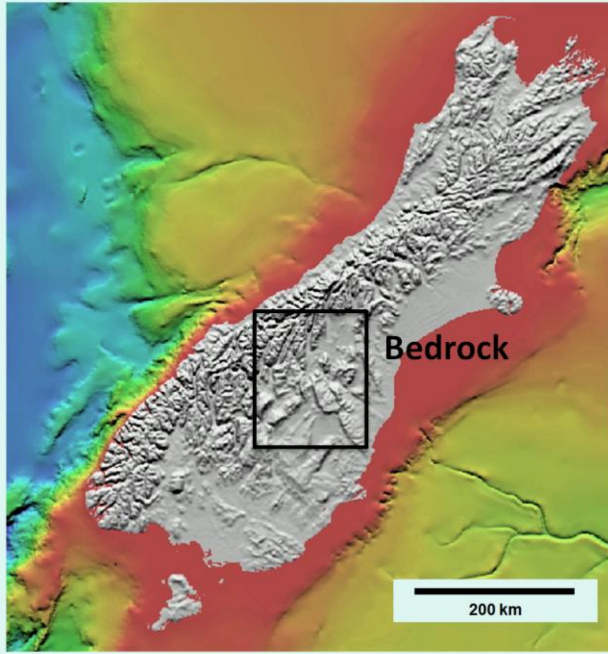
ave Ti (ppm)	exclusion
<	>
0.01	1000

	use?	corr factor
46Ti	**no**	**1**
47Ti	**yes**	**1**
48Ti	**no**	**1.6**
49Ti	**yes**	**1**
50Ti	**yes**	**1**



Case Studies

- bedrock sediment sources (greywacke grades into schist)

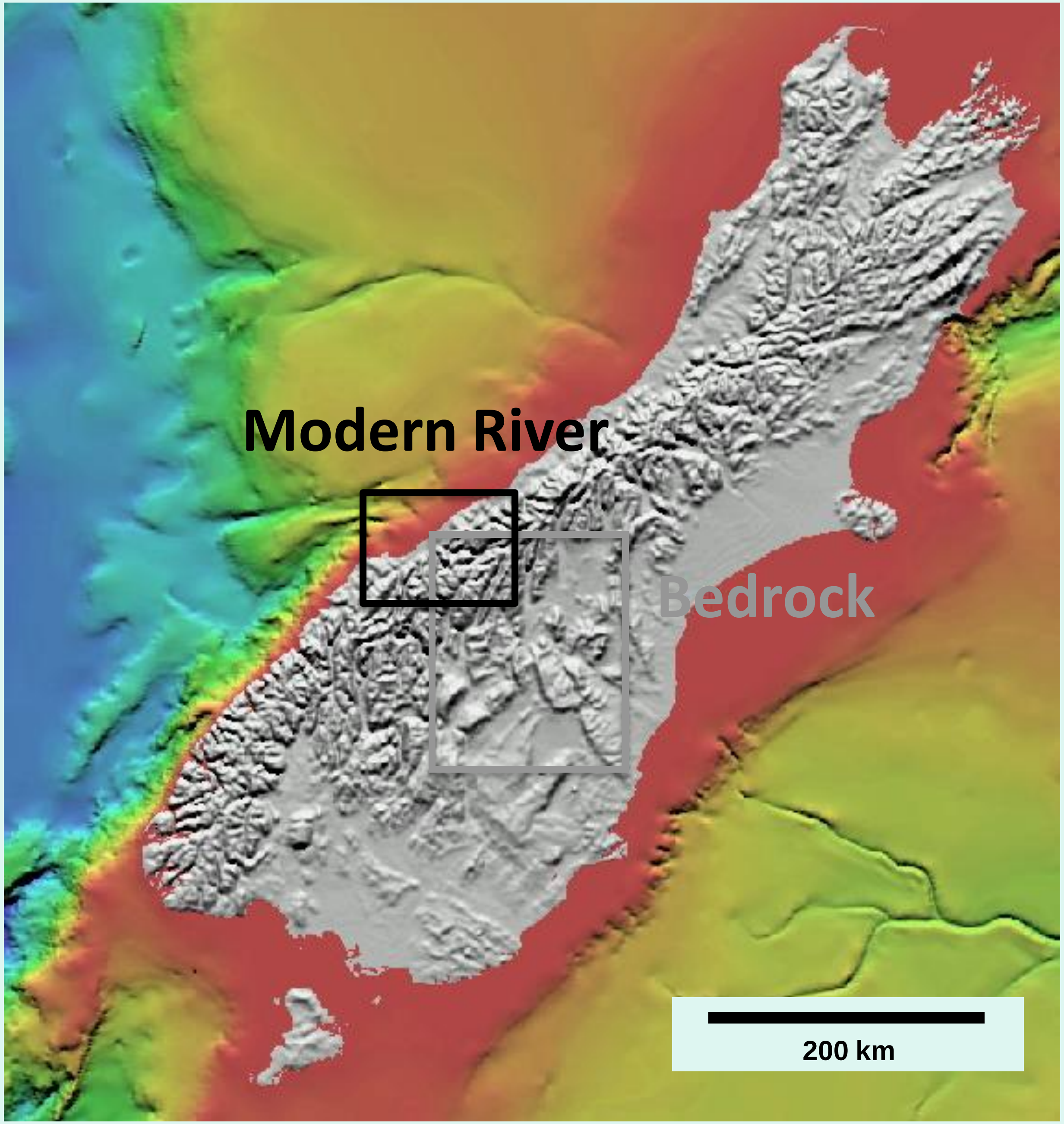


Presenter's notes: We have explored the use of Ti and other trace elements in detrital quartz as a "fingerprint" of sediment provenance in modern rivers and ancient basins of the South Island of New Zealand.

Case Studies

- bedrock sediment sources (greywacke grades into schist)

- modern river sediment

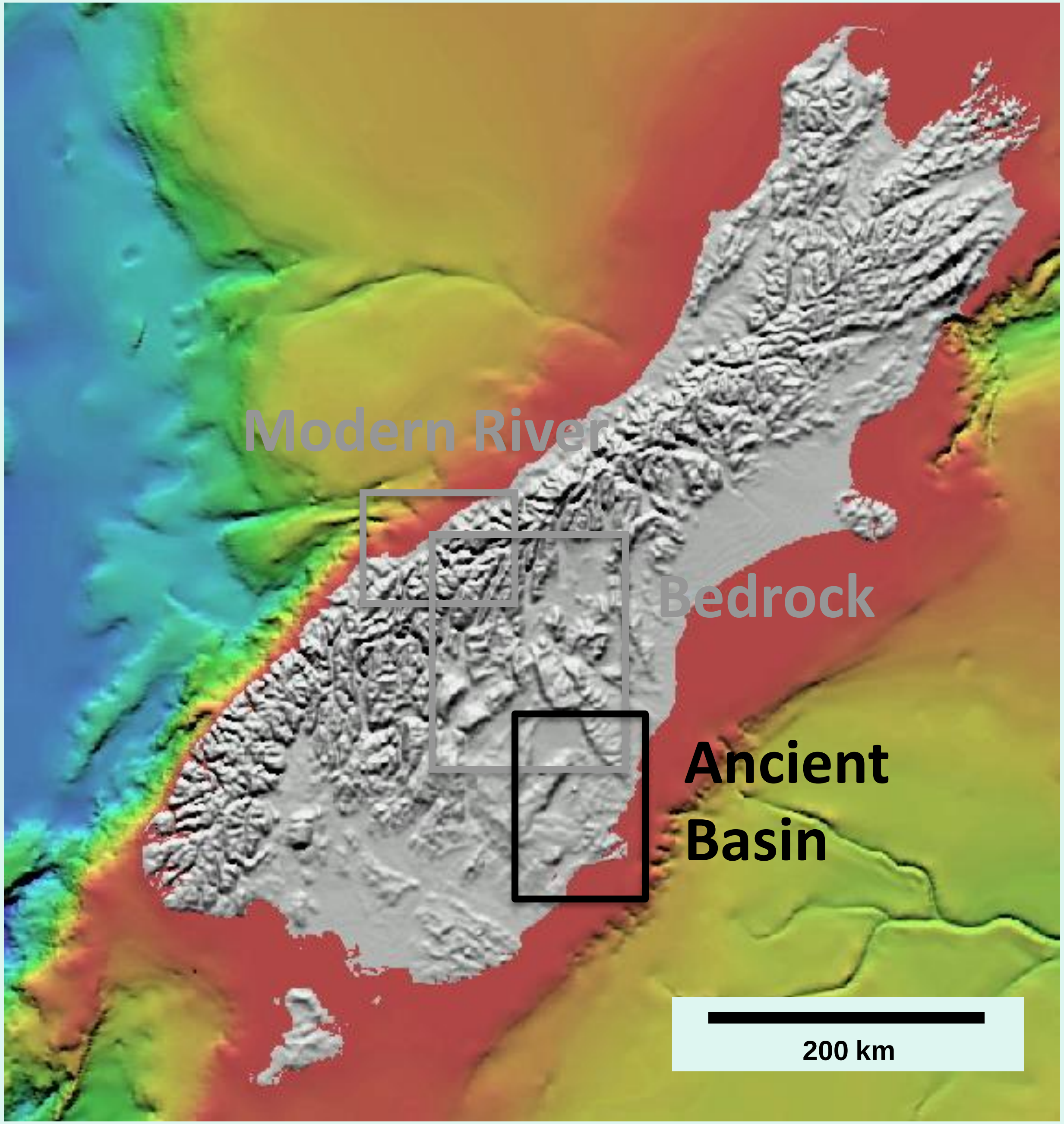


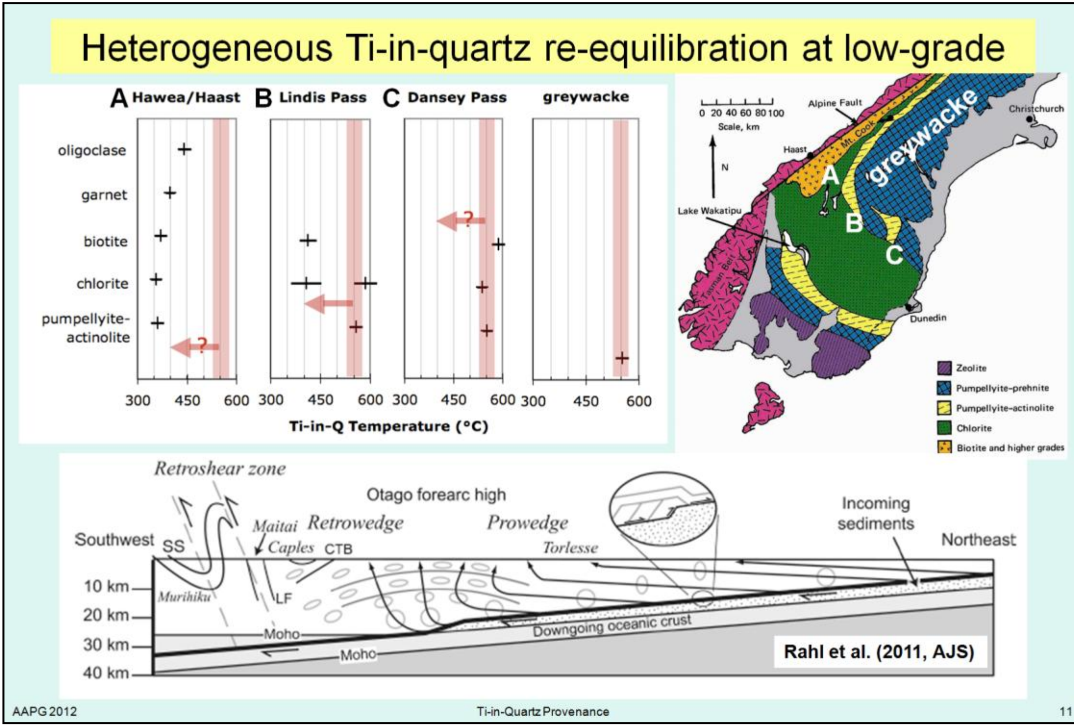
Case Studies

- bedrock sediment sources (greywacke grades into schist)

- modern river sediment

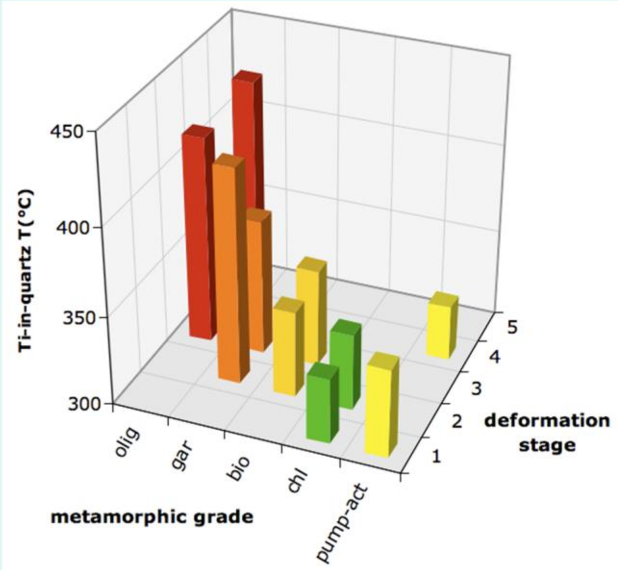
- ancient sedimentary basin deposits

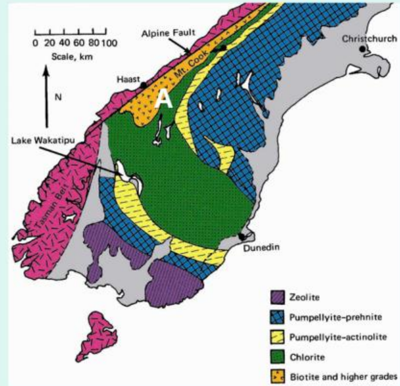




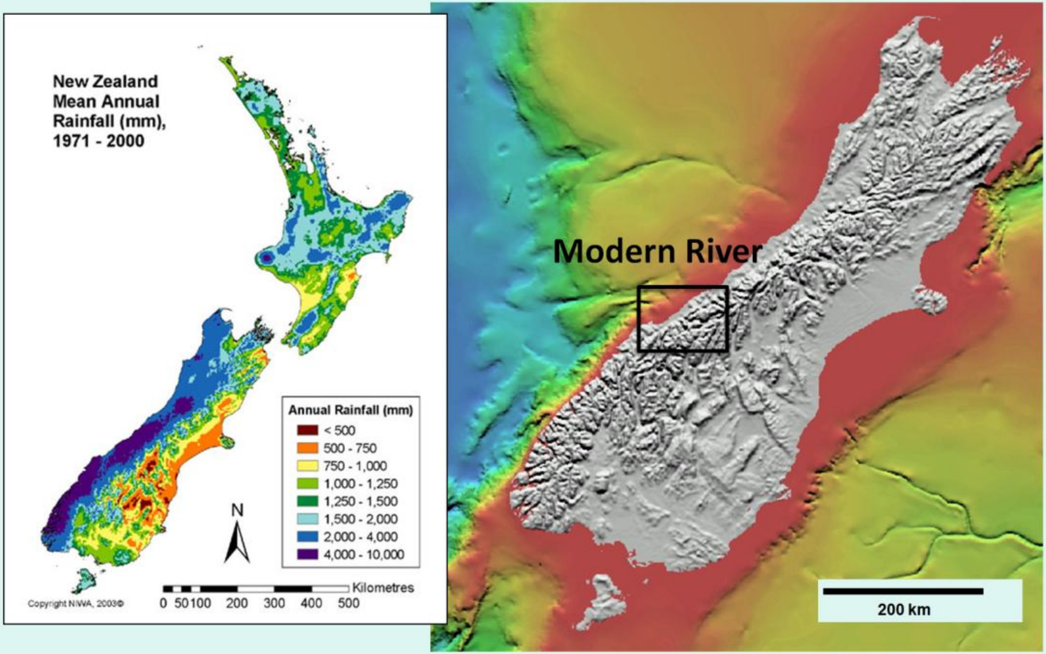
Presenter's notes: Detrital quartz in Permian-Jurassic greywacke sandstones exhibit uniformly high Ti concentrations that reflect plutonic sources. Regional metamorphism of these rocks has resulted in heterogeneous re-equilibration at lowest grade and…

Systematic re-equilibration of Ti-in-quartz at medium- to high-grade

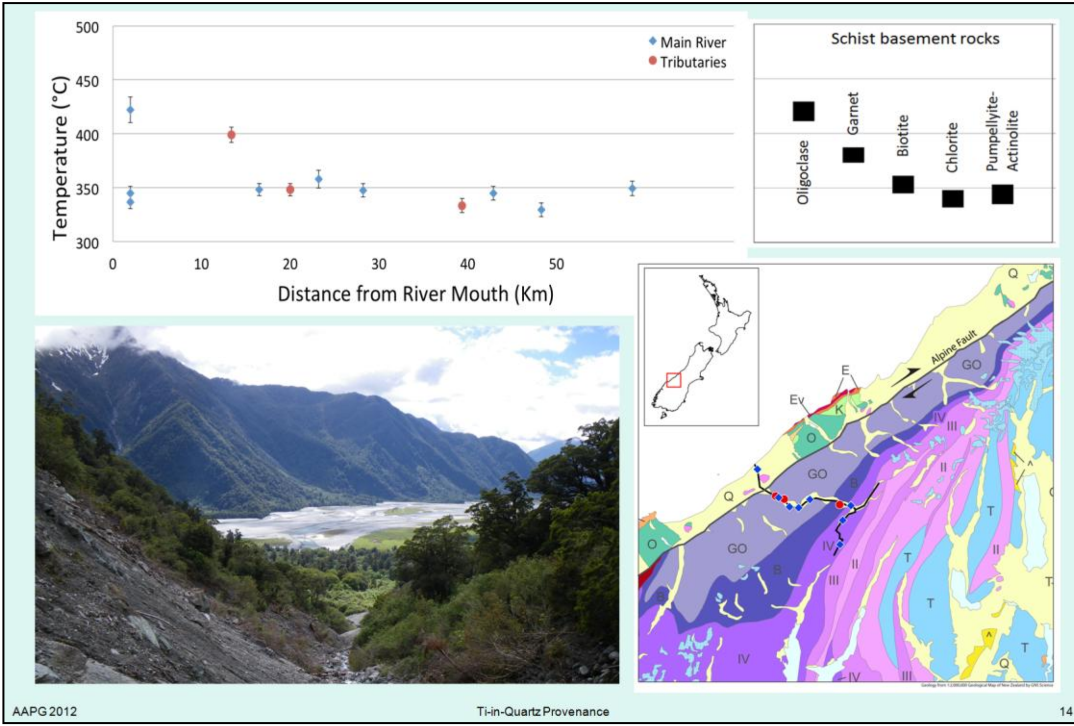




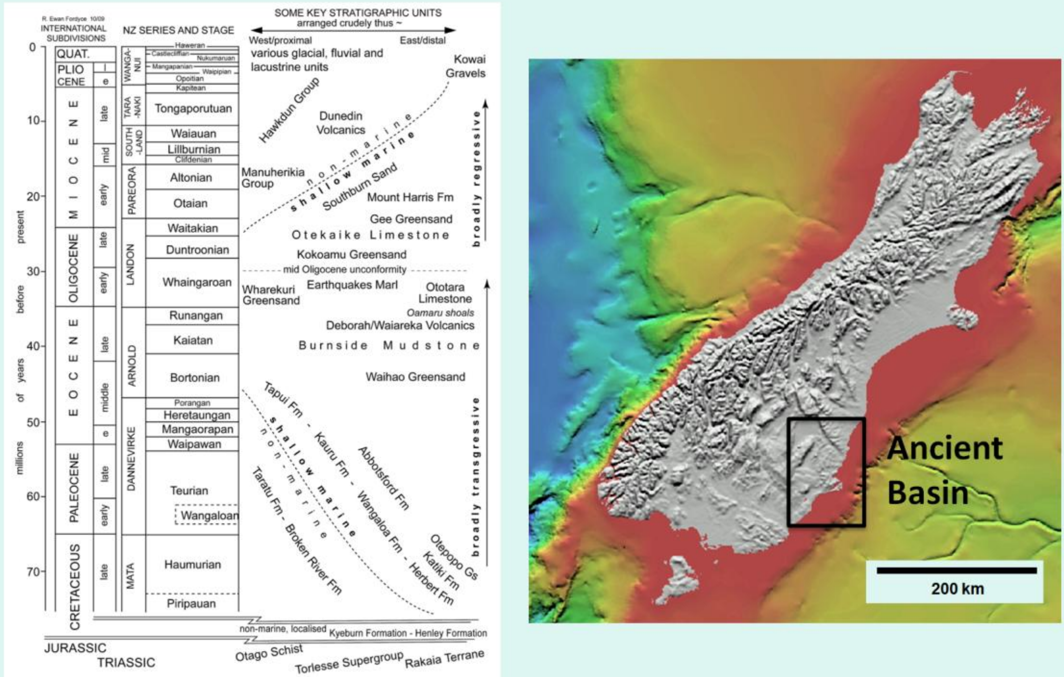
Presenter's notes: …systematic increases in quartz Ti concentrations that accompany recrystallization from medium- to high-grade. The latter provide metamorphic P-T estimates that agree with previous thermobarometry.



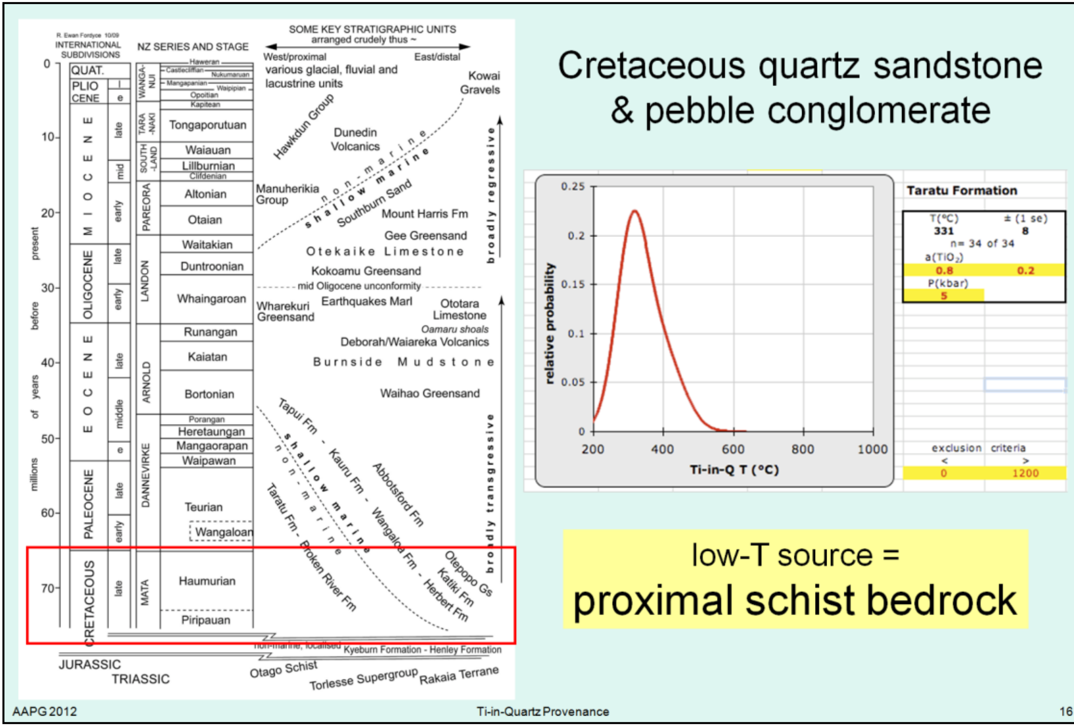
Presenter's notes: The Haast River drains the western slopes of the Southern Alps and is characterized by high sediment load.



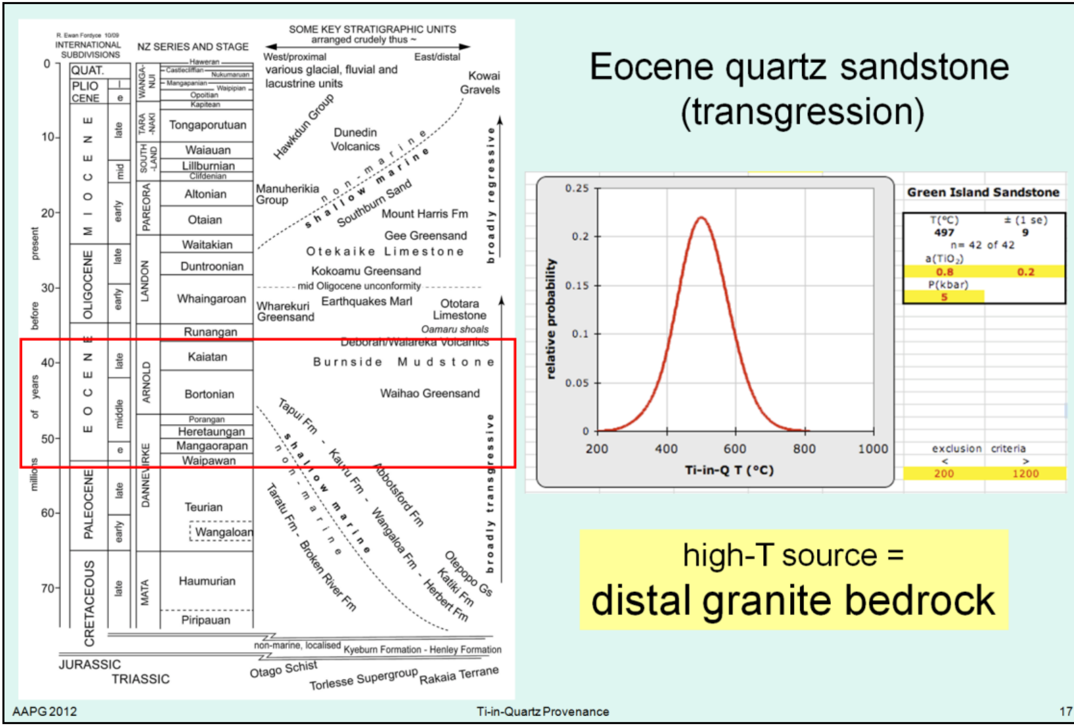
Presenter's notes: Quartz in bedload sediment from modern rivers that drain these metasedimentary rocks in the Southern Alps has Ti concentrations that correlate with metamorphic grade of upstream bedrock. Some samples exhibit smooth variation of quartz Ti concentrations with grain size that indicate hydrodynamic fractionation of sediment from heterogeneous sources.



Presenter's notes: Titanium concentrations in detrital quartz from Cretaceous-Neogene siliciclastic deposits of eastern Otago exhibit distinct shifts with age and location.

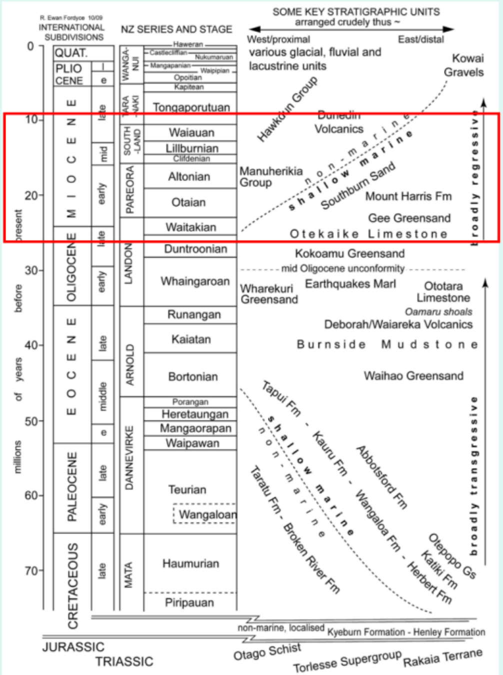


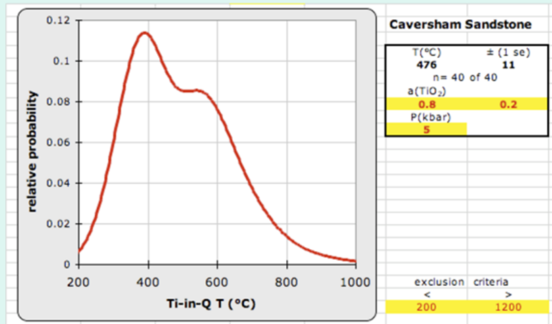
Presenter's notes: Cretaceous sandstones and conglomerates contain quartz with Ti concentrations that are consistent with derivation from local igneous and metamorphic bedrock.



Presenter's notes: Paleogene sandstones have quartz with higher Ti concentrations that require derivation from distal granitic or greywacke sources during marine transgression.

Miocene quartz sandstone (regression)





bimodal (low- & high-T) source =

reworked cover

Presenter's notes: Neogene samples contain quartz with a bimodal distribution of quartz having high and low Ti concentrations that probably reflect reworking of underlying deposits during marine regression.

Conclusion

Ti-in-quartz can be a powerful complement to other means of provenance determination* for siliciclastic sediments provided the sources are distinctive

*framework & heavy mineral modes, quartz CL, zircon U-Pb ages, feldspar Pb isotopes