Assessing seasonal controls in silicon cycle and isotopic signatures of groundwater under anthropogenic stress in tropical watershed

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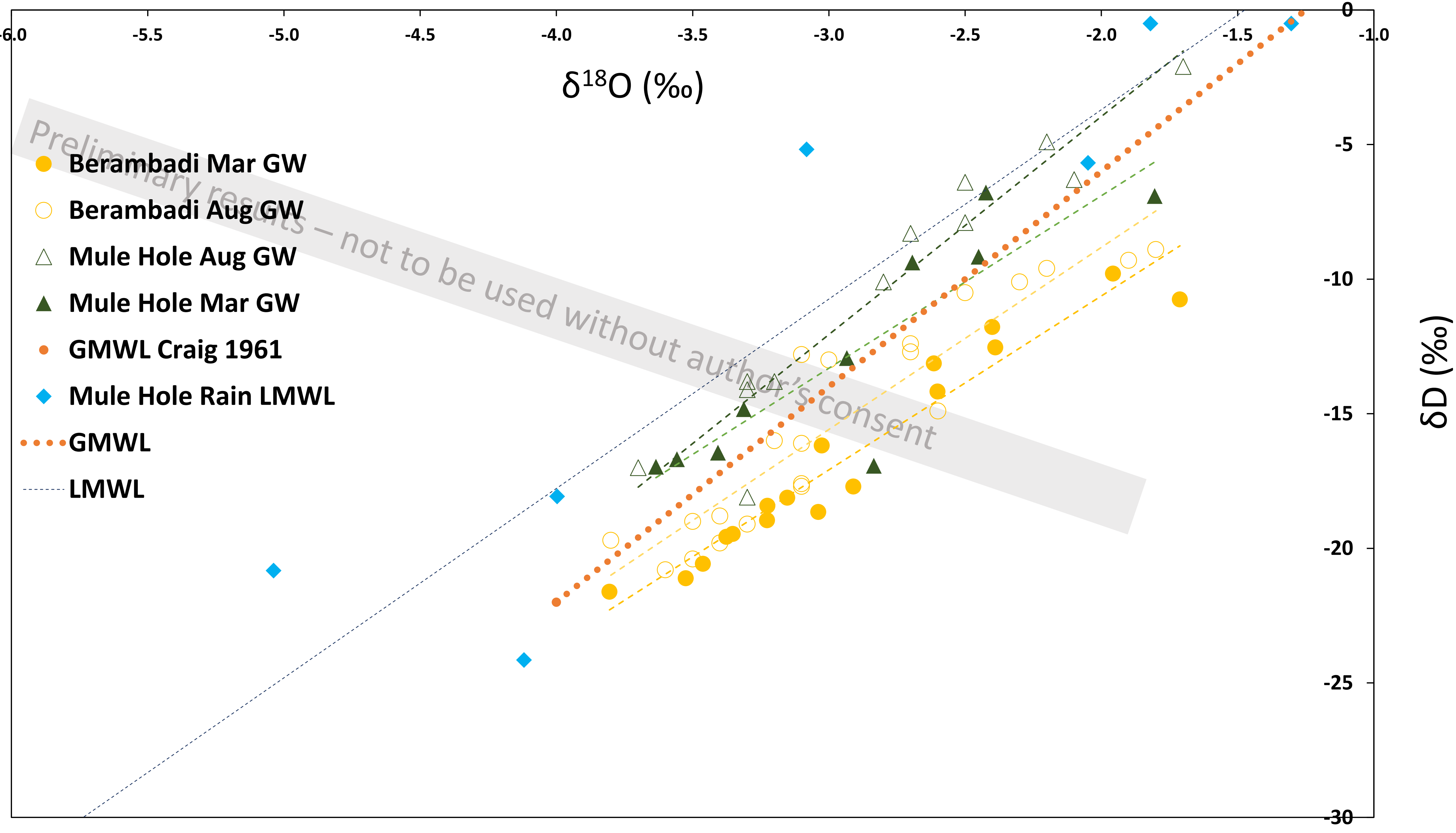
Sampling sites (South India)

Image showing three sampling locations, a) Godavari basin in Andhra Pradesh, b) Berambadi aa agricultural catchment and c) Mule Hole a pristine forested catchment, both in Karnataka.

Fig 1. The $\delta^{18}O$ vs δD plot for the groundwater and rainwater samples



Sampling Site	Season	Equation	R^2
Berambadi GW	March	$\delta D = 6.46\ (\pm 0.4) * \delta^{18}O + 2.30\ (\pm 1.2)$	*0.94*
	August	$\delta D = 6.60\ (\pm 0.6) * \delta^{18}O + 3.85\ (\pm 1.8)$	*0.86*
Mule Hole GW	March	$\delta D = 6.41\ (\pm 1.2) * \delta^{18}O + 5.91\ (\pm 3.6)$	*0.77*
	August	$\delta D = 8.44\ (\pm 0.9) * \delta^{18}O + 13.35\ (\pm 2.6)$	*0.92*
Mule Hole Rainwater (LMWL)		$\delta D = 7.04\ (\pm 0.3) * \delta^{18}O + 10.37\ (\pm 2.1)$	*0.97*
Global Meteoric Water Line (GMWL)		$\delta D = 8 * \delta^{18}O + 10$ *(Craig, 1961)*	

Table 1. The $\delta^{18}O$ vs δD relationship for the groundwater samples and the LMWL along with the R^2 value.

Water Isotopes in Groundwater

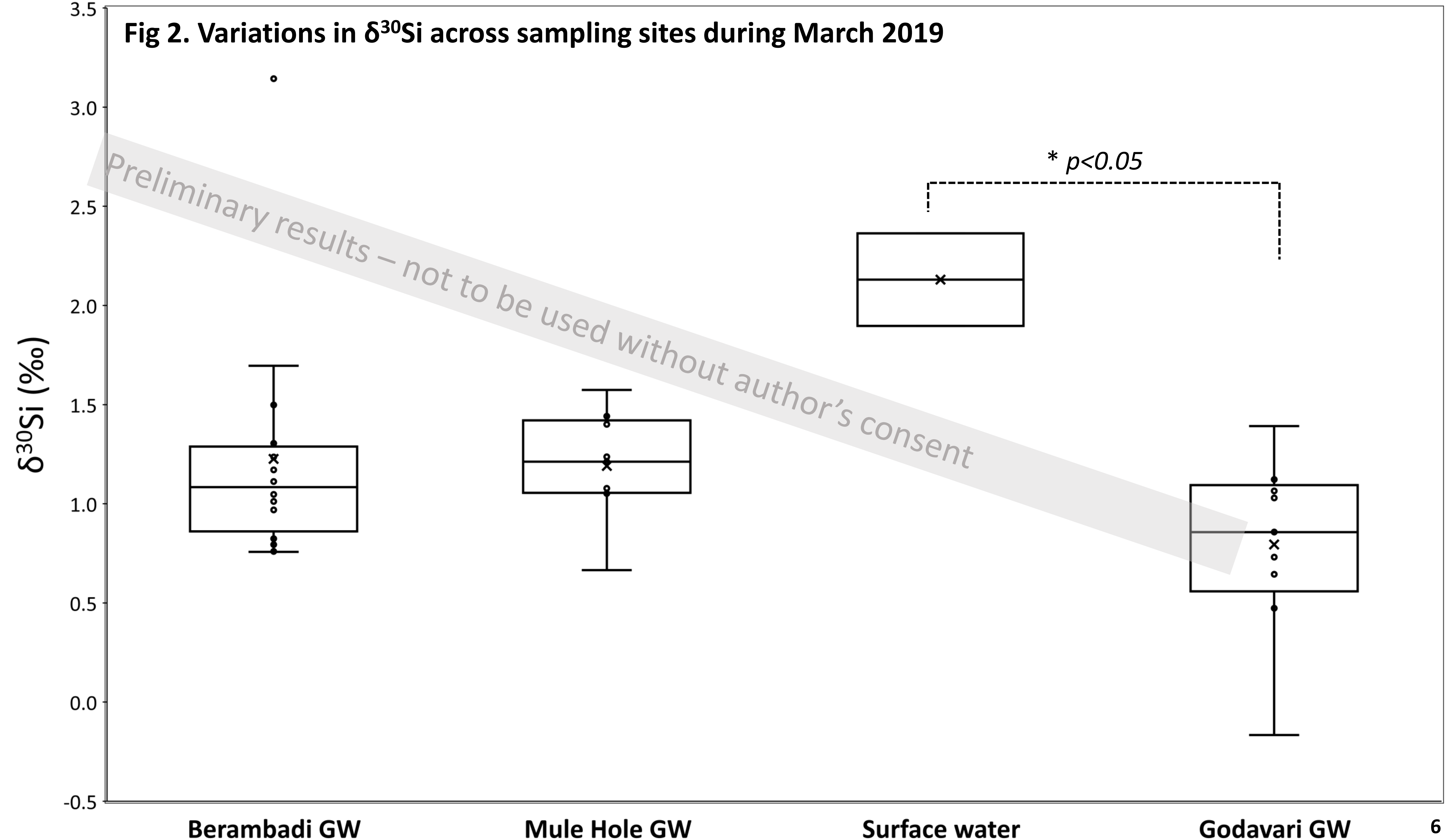
- Stable isotope of water molecule was investigated to understand the groundwater recharge process i.e. monsoon input under two land use conditions; higher water use through irrigation in an agricultural region and a tropical forest watershed.

- The $\delta^{18}O$ values ranges between -2 and -4 ‰ for groundwater whereas the rain water displayed a wider range from -1 to -12 ‰. Local Meteoric Water Line (LMWL) include rain water collected during July, August, September, October and January from Mule Hole.

- Except the Mule Hole August, slope of $\delta^{18}O$ vs. δD values for all groundwater samples closely followed LMWL indicating a direct recharge from local present day precipitation.

- Significantly lower intercept (d-excess) values (<5‰) in the samples from Berambadi (cultivated) Mar, Aug and Mule Hole (Dry forest) Mar is due to kinetic evaporation during groundwater recharge *(Négrel et al 2011).* Extensive irrigation in the cultivated region leads to irrigation return flow which can cause higher evaporation in both seasons and lower d excess value compared to Mule Hole.

Fig 2. Variations in $\delta^{30}Si$ across sampling sites during March 2019



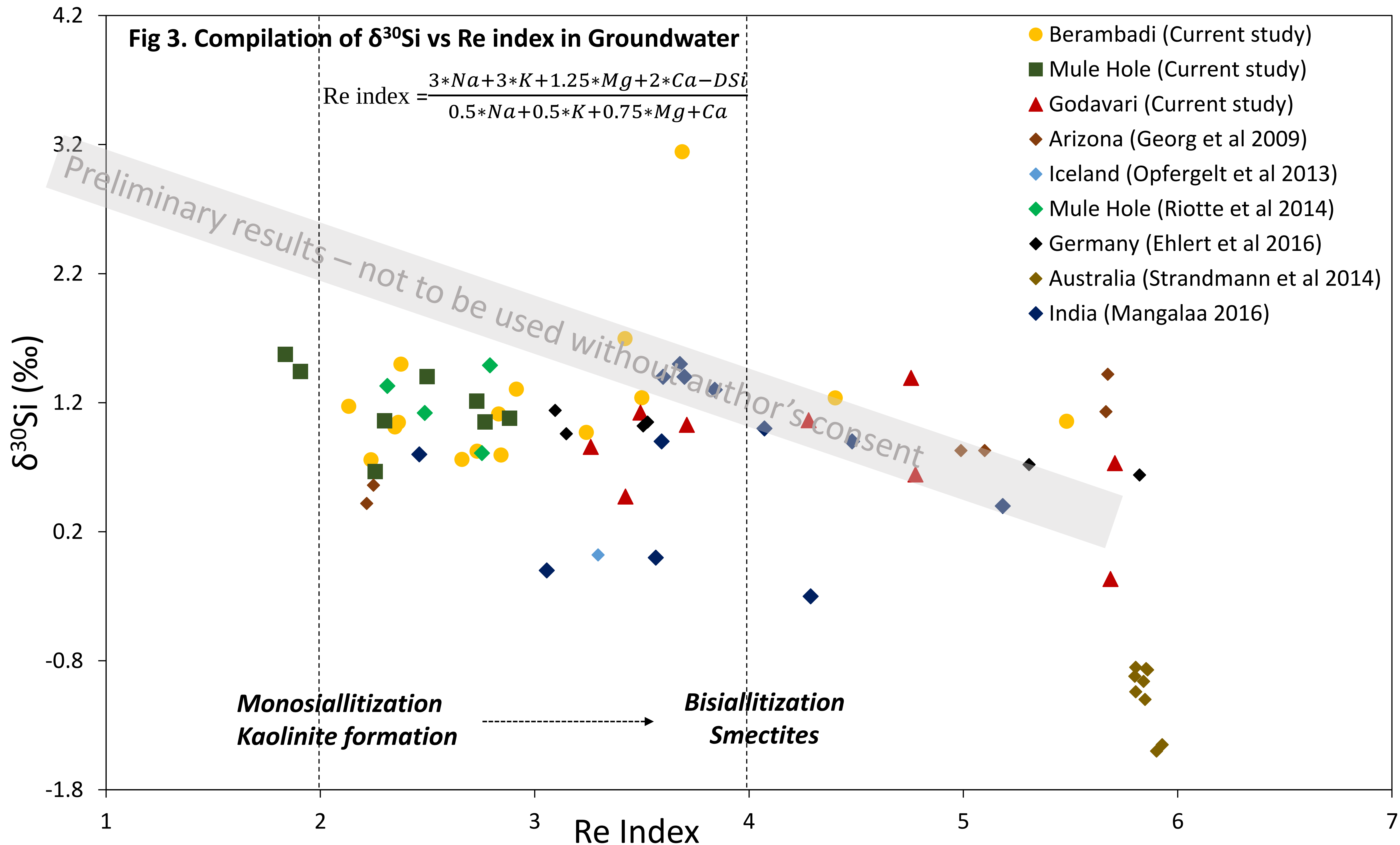


Fig 3. Compilation of δ30Si vs Re index in Groundwater
Re index = 3*Na+3*K+1.25*Mg+2*Ca−DSi / 0.5*Na+0.5*K+0.75*Mg+Ca
Berambadi (Current study)
Mule Hole (Current study)
Godavari (Current study)
Arizona (Georg et al 2009)
Iceland (Opfergelt et al 2013)
Mule Hole (Riotte et al 2014)
Germany (Ehlert et al 2016)
Australia (Strandmann et al 2014)
India (Mangalaa 2016)
Preliminary results – not to be used without author's consent
Monosiallitization
Kaolinite formation
Bisiallitization
Smectites
δ30Si (‰)
Re Index
4.2
3.2
2.2
1.2
0.2
-0.8
-1.8
1
2
3
4
5
6
7

Si isotopes in Groundwater and Weathering

- Groundwater samples from Berambadi and Mule Hole collected during August doesn't show any significant difference in the $\delta^{30}Si$ values. Surface water $\delta^{30}Si$ values were slightly heavier compared to groundwater data.

- Groundwater from Mule hole had a similar range in $\delta^{30}Si$ and lower Re index values (2.3) to that of earlier study from the same region by *Riotte et al 2014,* while Godavari sample mostly confined to higher Re index (4.3) and Berambadi (3.1) ranged in between.

- Preliminary data suggest no significant differences between the $\delta^{30}Si$ of groundwater from forested catchment (Mule Hole) and intensely cultivated catchment (Berambadi).

- Compilation of all groundwater silicon isotope data shows no correlation with weathering intensity proxies such as Re index, DSi/(Na+K), DSi/Na and DSi (not shown) unlike the data from surface water samples reported by *Mangalaa Thesis 2016 and Frings et al 2016.*

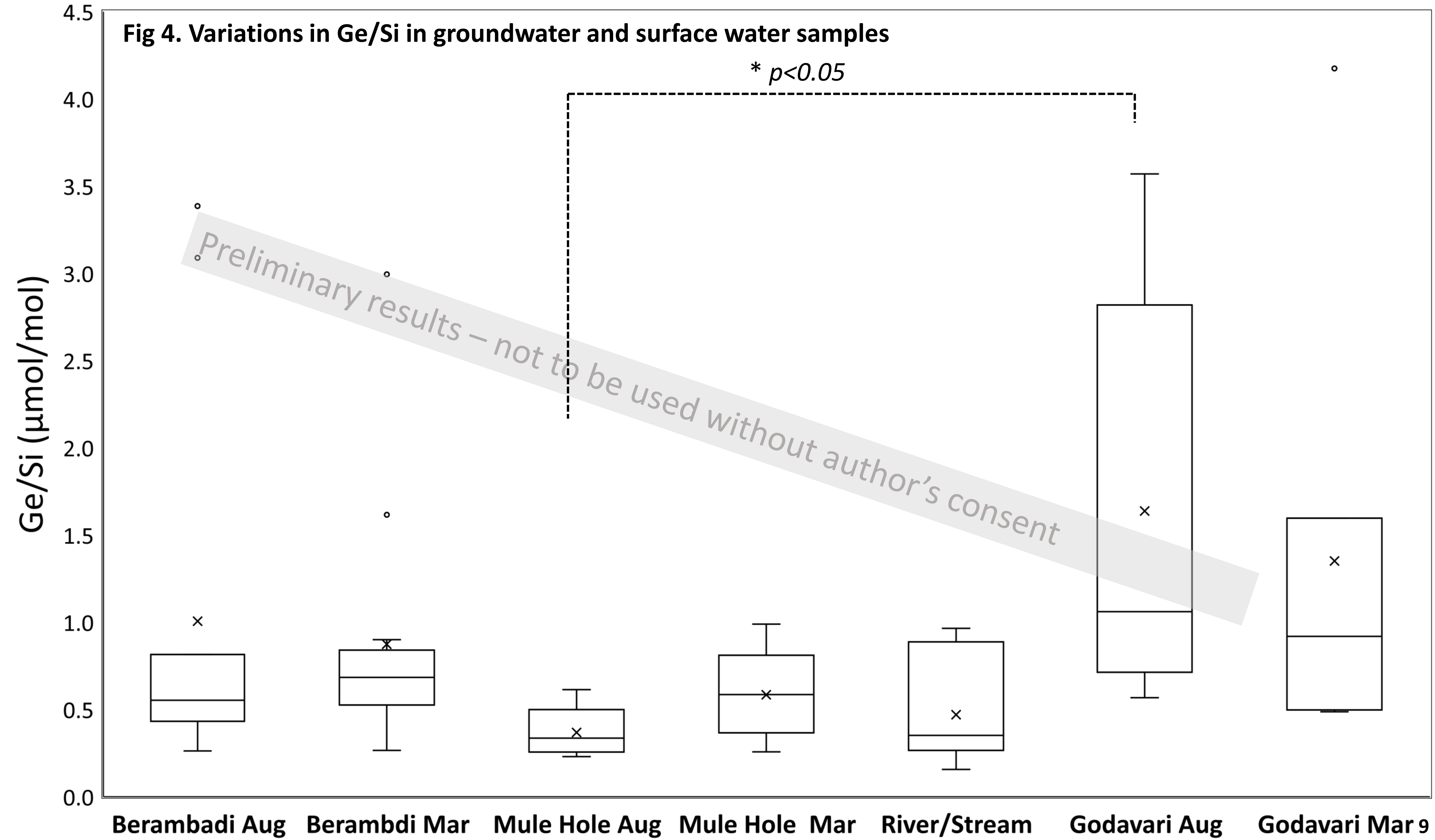


Fig 4. Variations in Ge/Si in groundwater and surface water samples
* p<0.05
Preliminary results – not to be used without author's consent
Ge/Si (µmol/mol)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Berambadi Aug
Berambdi Mar
Mule Hole Aug
Mule Hole Mar
River/Stream
Godavari Aug
Godavari Mar

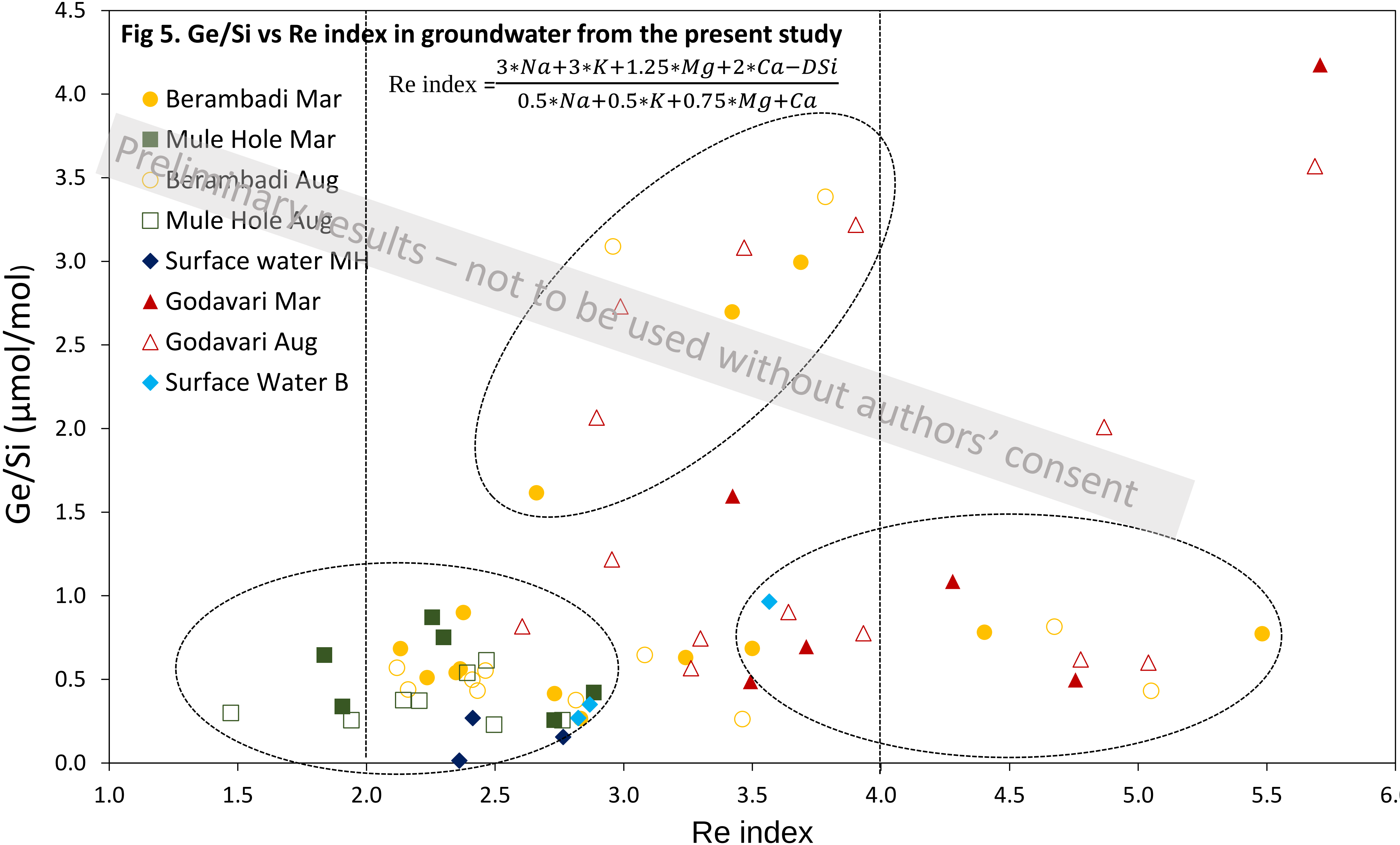


Fig 5. Ge/Si vs Re index in groundwater from the present study
Re index = $\frac{3*Na+3*K+1.25*Mg+2*Ca-DSi}{0.5*Na+0.5*K+0.75*Mg+Ca}$
Berambadi Mar
Mule Hole Mar
Berambadi Aug
Mule Hole Aug
Surface water MH
Godavari Mar
Godavari Aug
Surface Water B
Preliminary results – not to be used without authors' consent
Ge/Si (µmol/mol)
Re index
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0

Ge/Si ratio in groundwater

- Ge/Si ratio in groundwater varied from 0.4 to 4.2 mmol/mol, and the surface water had lower values ranging from 0.1 to 0.96 mmol/mol.

- There is no significant differences in Ge/Si ratio between groundwater from highly irrigated Berambadi region and forested Mule Hole watershed. We also didn't observe any seasonal variability between the groundwater samples from three sites.

- Weathering products such as secondary minerals (clays) and iron oxy-hydroxides are enriched in Ge compared to primary rock making Ge/Si a proxy for weathering intensity.

- All the groundwater samples from Mule Hole showed a lower Re index (<3) and Ge/Si ratio (<1), but the Berambadi and Godavari groundwater showed two distinct patterns; one with intermediate Re index (2.5-4) and higher Ge/Si ratio (1.5-3.5) and another with high Re index (>3.5) and lower Ge/Si ratio (<1).

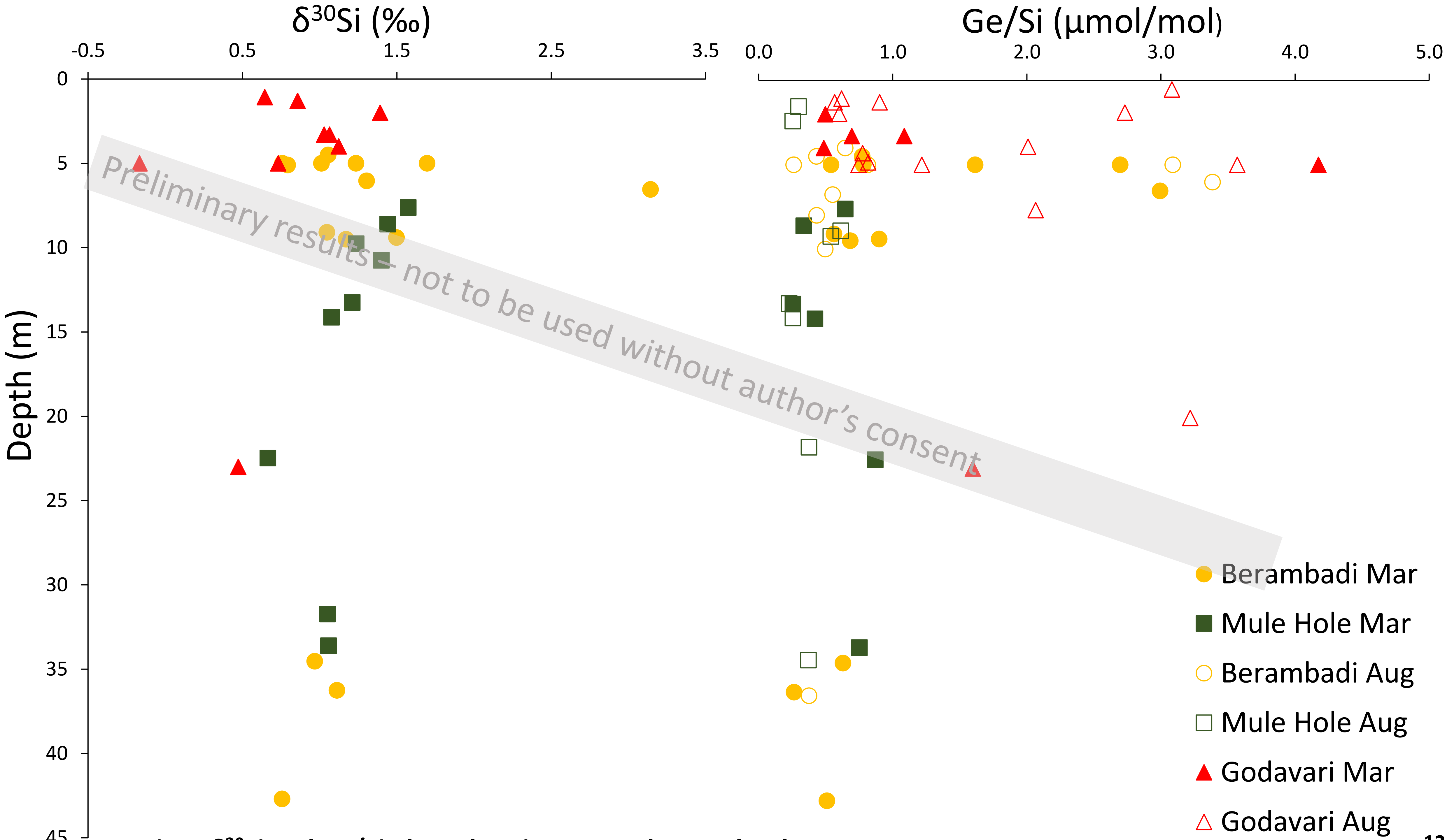


Fig 6. δ^{30}Si and Ge/Si plotted against groundwater depth

Conclusion and Future works

- Preliminary results suggest no significant difference in Si isotopes values and Ge/Si ratio between groundwater from agricultural and forested catchment.

- δ^{30}Si values were lighter for groundwater compared to surface water from the region but no significant variations were observed in between study sites. δ^{30}Si also values showed greater variations for shallow groundwater (<10m) and a lower confined value for the deeper.

- Preliminary results of groundwater analysis from Berambadi (cultivated), Mule Hole (forested) and Godavari sampled during March revealed no correlation between δ^{30}Si and Ge/Si ratio. We are yet to perform δ^{30}Si measurement of groundwater and surface water samples in August from all three study sites.

- Further analysis including Sr and Ca isotopes together with major and trace element data would refine our understanding of Si biogeochemistry in groundwater and the changes associated with land use.

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