

# Ultrahigh amounts of sodium in the ringwoodite structure

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# What about the sodium preference at high pressure?



*The solubility of Na in high-pressure minerals as well as their abundance under the conditions of the upper mantle and transition zone attract considerable interest of experimentalists and mineralogists.*

$\text{Na}_2\text{Si}(\text{Si}_2\text{O}_7)$  (Fleet and Henderson 1995)

$\text{Na}_{1.8}\text{Ca}_{1.1}\text{Si}_6\text{O}_{14}$  (Gasparik et al. 1995)

$\text{Na}_6\text{Si}_3(\text{Si}_9\text{O}_{27})$  (Fleet 1996)

$\text{Na}_8\text{Si}(\text{Si}_6\text{O}_{18})$  (Fleet 1998)

$\text{Na}_2\text{Mg}_{4+x}\text{Fe}_{3+2-2x}\text{Si}_{6+x}\text{O}_{20}$  (Gasparik et al. 1999)

$(\text{K},\text{Na})_{0.9}(\text{Mg},\text{Fe})_2(\text{Mg},\text{Fe},\text{Al},\text{Si})_6\text{O}_{12}$  (Gasparik et al. 2000)

$\text{Na}(\text{Mg}_x\text{Si}_x\text{Al}_{1-2x})\text{Si}_2\text{O}_6$  ( $0 \leq x \leq 0.5$ ) (Yang et al. 2009)

$\text{Na}_2\text{MgSi}_5\text{O}_{12}$  (Bindi et al. 2011)

**Na-garnet:  $^{\text{VIII}}\text{Mg}^{2+} + ^{\text{VI}}\text{Al}^{3+} \rightarrow ^{\text{VIII}}\text{Na}^+ + ^{\text{VI}}\text{Si}^{4+}$**



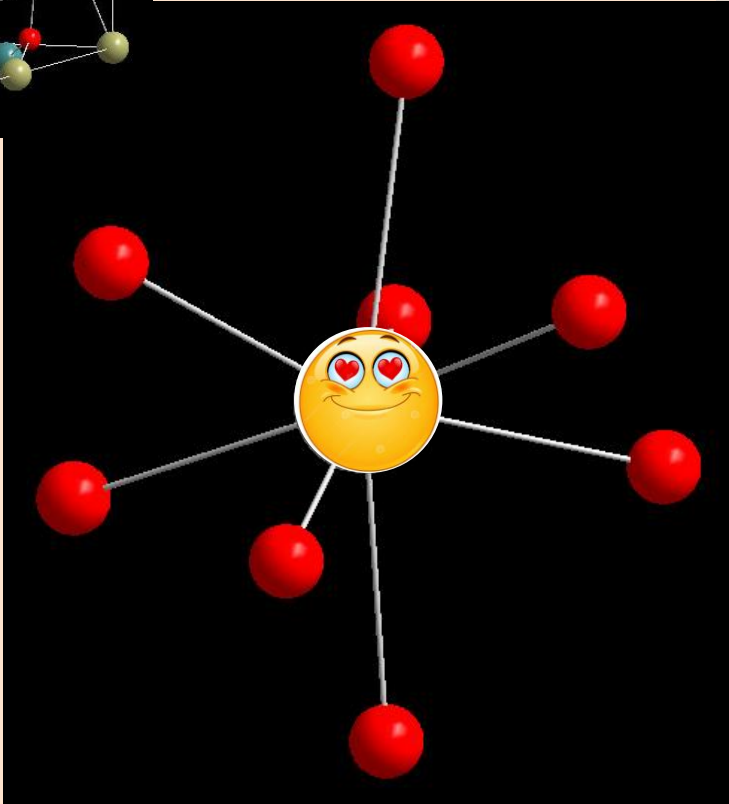
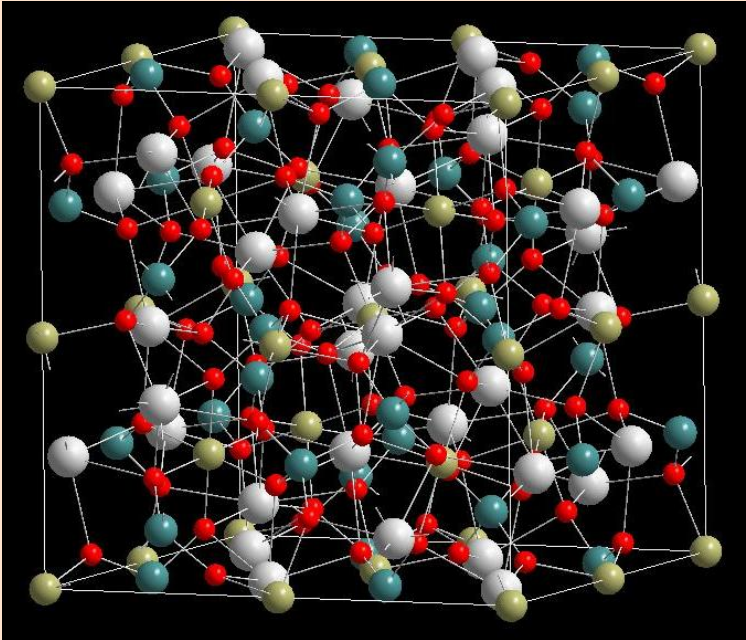
Na-bearing  
majoritic garnet  
was found as an  
inclusion in  
diamond in  
many kimberlitic  
pipes



and especially because...

...Na loves the large 8-fold coordinated site of the garnet structure

Ionic radius  
1.18 Å  
in  
eight-fold  
coordination





**Can you force  
Na to enter  
the  
octahedral  
site  
of a more  
compact  
structure?**

**Like the  
spinel  
structure?**

We had the same problem 15 years ago to demonstrate that K could enter the clinopyroxene structure...

*(see Safonov, Bindi and Vinograd 2011, MM 75, 2467 for a comprehensive review)*

### The «Men On the Bench» (MOB) model:

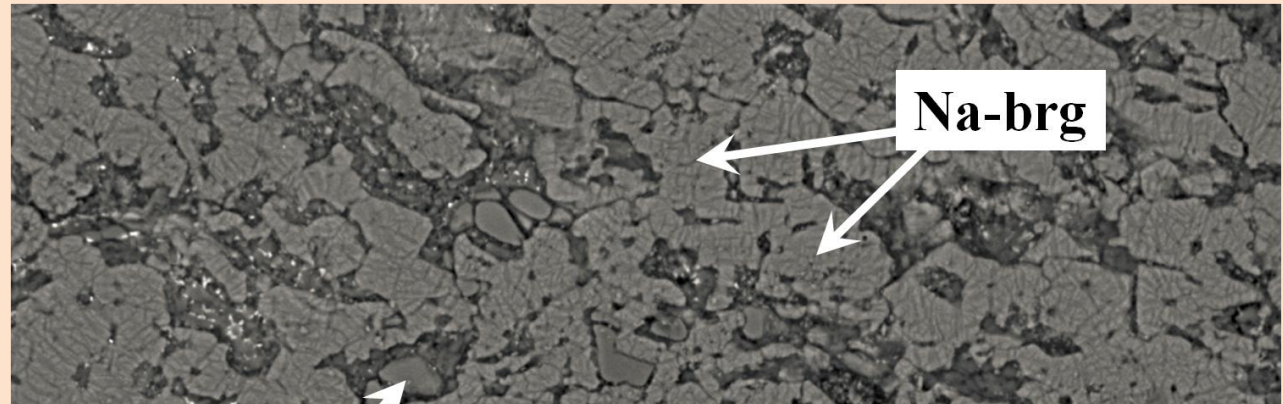
*Like a bench fully occupied during the lunch time, where it is easier for a large guy to get a seat if he can squeeze in adjacent to small people, the large Na cation can enter a site in the constrained structure of a spinel if there are smaller adjacent cations so the average size is not too large.*

*The large Na cation could be incorporated in the spinel structure provided some smaller cations (e.g. Si) were present so as to reduce the average cation size*

The  
experiment  
succeeded  
at the  
beginning  
of 2015

Experiment done at  $P = 24$  Gpa,  $T = 1700$  °C (Matsuyama, Japan).  
Starting materials:  $\text{MgSiO}_3$  (70 mol%) +  $\text{Na}_2\text{CO}_3$  (20 mol%) +  $\text{Al}_2\text{O}_3$   
(5 mol%) +  $\text{MgO}$  (5 mol%).

The roughly estimated proportions of the phases (by SEM area fractions; in vol. %) are: bridgmanite (75), ringwoodite (15), Na-free periclase (5), carbonate-silicate melt (5).

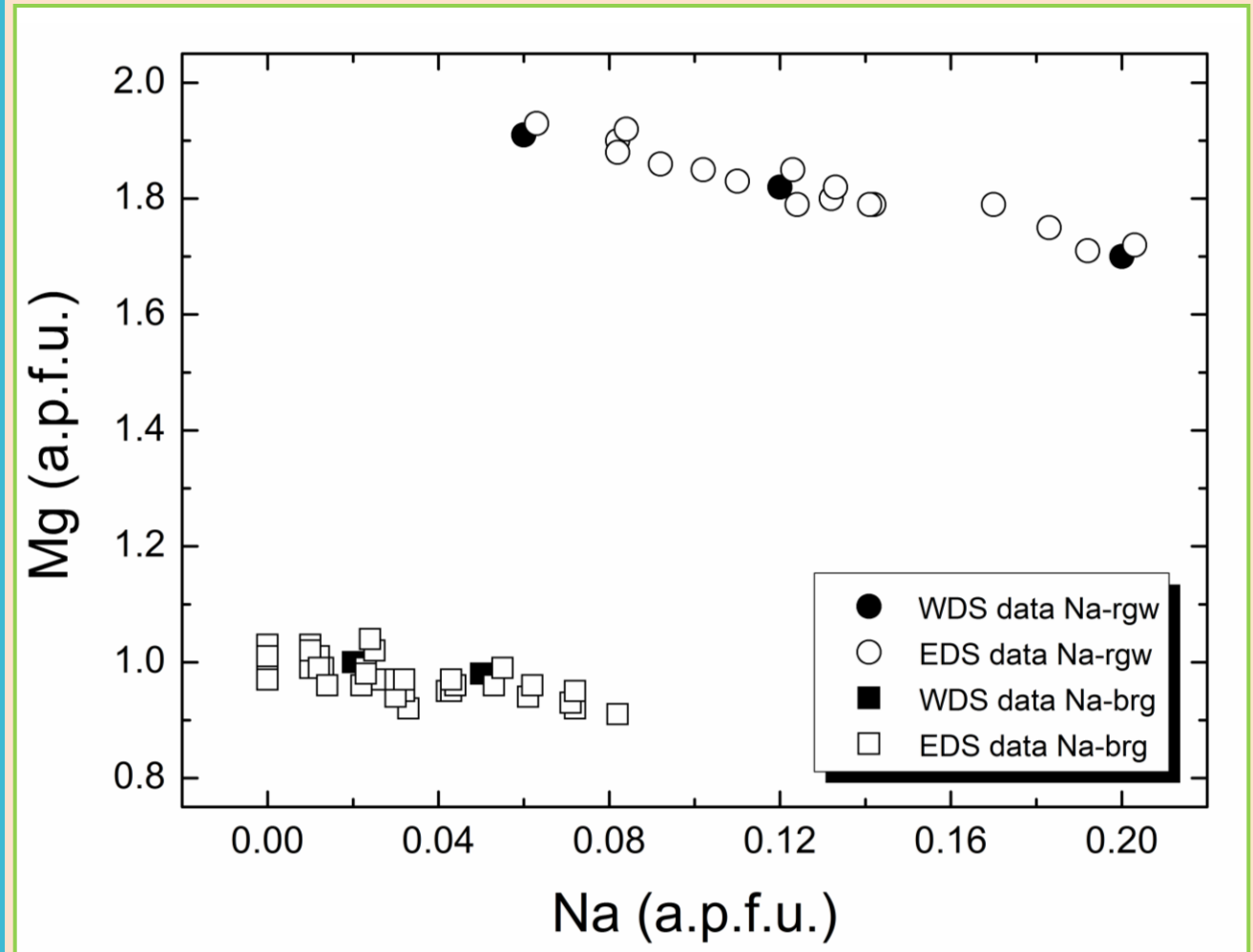


*The experiment was carried out by **Anastasia Tamarova** and conceived with **Ekaterina Sirotkina** and **Andrey Bobrov**, with the supervision of **Tetsuo Irifune***



**Na-ringwoodite with up to 4.4 wt% of Na<sub>2</sub>O**  
**Na-bridgmanite with up to 1.5 wt% of Na<sub>2</sub>O**

**What can we infer from the chemical data?**



associated with Na-free periclase and melt with composition: 21.7(2) (Na<sub>2</sub>O), 20.7(1) (MgO), 2.29(3) (SiO<sub>2</sub>), 1.32(4) (Al<sub>2</sub>O<sub>3</sub>) and 54.0(3) (CO<sub>2</sub>)

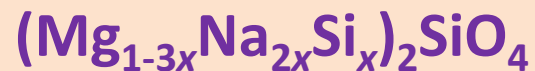
## Electron microprobe data

How we can write the formula of Na-rich ringwoodite?

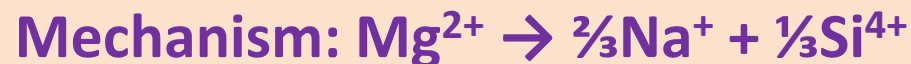
And, is it really true the «MOB» model?

	Na-rgw1	Na-rgw2	Na-rgw3	Na-brg1	Na-brg2
SiO <sub>2</sub>	45.68(21)	45.12(26)	44.03(25)	56.84(20)	59.60(23)
Al <sub>2</sub> O <sub>3</sub>	n.d.	n.d.	n.d.	2.62(9)	1.39(4)
MgO	48.28(22)	51.97(17)	54.78(23)	38.84(15)	38.24(18)
FeO	n.d.	n.d.	n.d.	n.d.	n.d.
Na <sub>2</sub> O	4.38(11)	2.63(9)	1.32(10)	1.54(7)	0.52(6)
Tot	99.24	99.72	100.13	99.83	99.75
Si	1.10(2)	1.06(2)	1.03(2)	0.96(3)	0.95(3)
Al	-	-	-	0.05(2)	0.03(2)
Mg	1.70(1)	1.82(2)	1.91(1)	0.98(2)	1.00(2)
Fe	-	-	-	-	-
Na	0.20(2)	0.12(3)	0.06(2)	0.05(2)	0.02(2)

the formula of Na-ringwoodite can be written as



with  $x = 0.050$ ,  $0.030$  and  $0.015$ , for Na-rgw1, Na-rgw2 and Na-rgw3, respectively.





How we can prove that Na really enters the octahedral site of the spinel structure? Does it really coexist with silicon?

## X-ray single crystal study



- The mean electron number at the sites
- The polyhedral geometry



Very powerful but...

How we can prove that Na really enters the octahedral site of the spinel structure? Does it really coexist with silicon?

Na-rgw1:



What about the mean electron number at the octahedral site?

$$[0.85 \times 12 + 0.10 \times 11 + 0.05 \times 14] = 12.00 e^-$$

(exactly as for a full occupation of Mg)

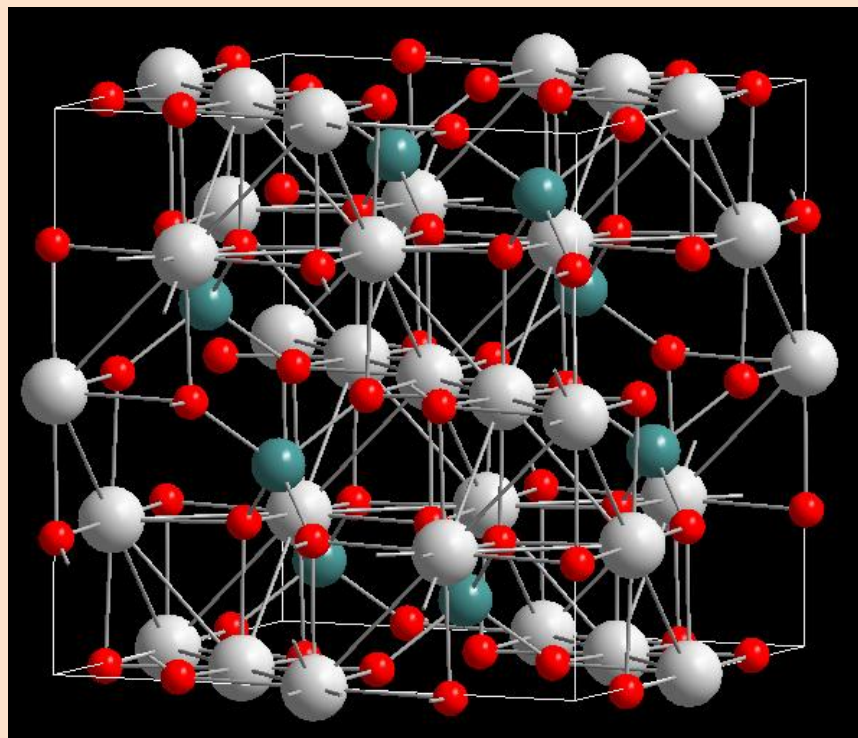


What about the geometry of the unit cell and the octahedral site?

Cubic unit-cell par. of pure  $\text{Mg}_2\text{SiO}_4 = 8.0816(1) \text{ \AA}$  (Ye et al. 2012)

Cubic unit-cell par. of Na-rich  $\text{Mg}_2\text{SiO}_4 = 8.0952(3) \text{ \AA} !!!$

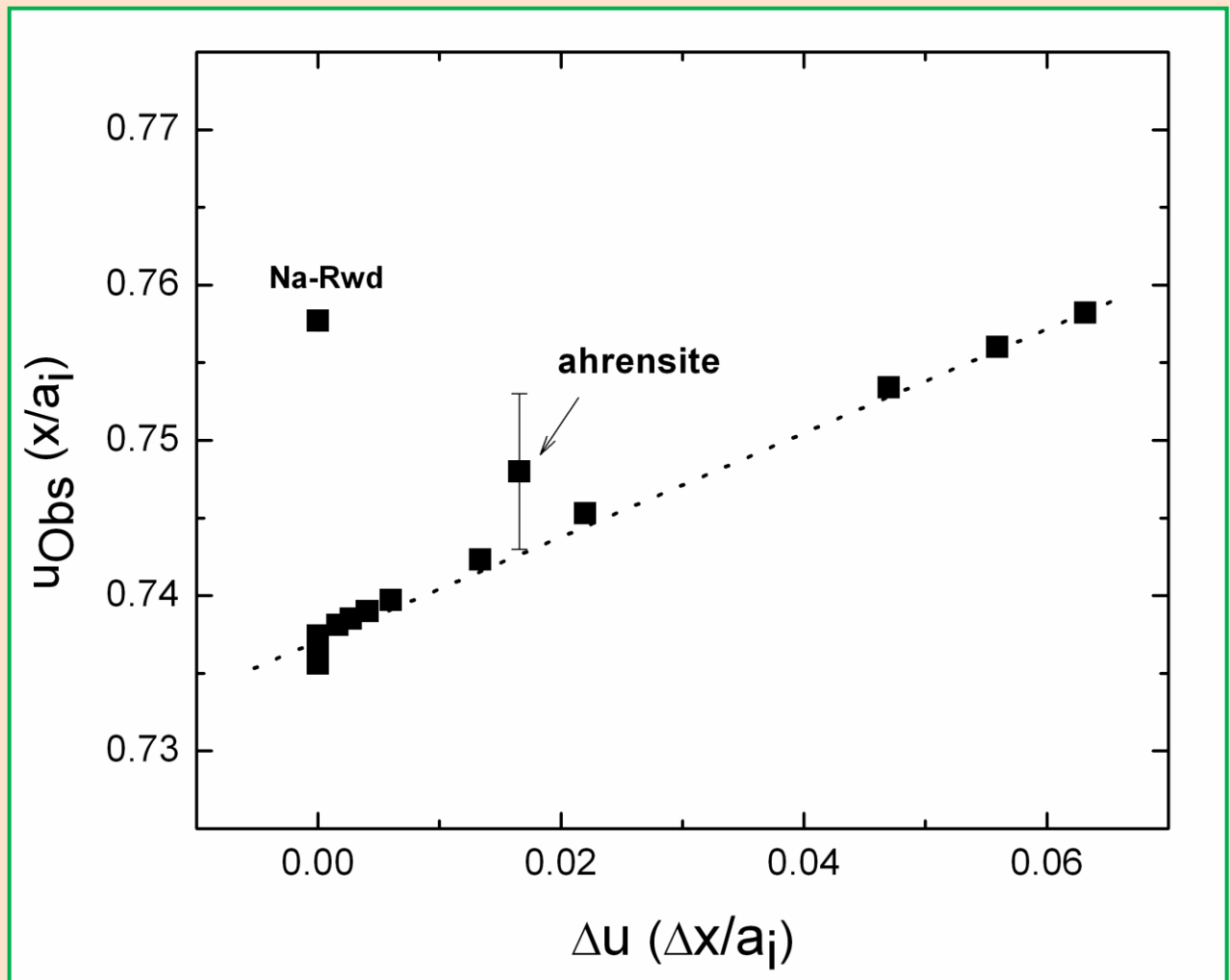
# The ringwoodite structure



	<i>x</i>	<i>y</i>	<i>z</i>	$U_{iso}/U_{eq}$
Mg	1/2	1/2	1/2	0.0093(3)
Si	1/8	1/8	1/8	0.0106(3)
O	0.24234(17)	0.24234(17)	0.24234(17)	0.0204(6)

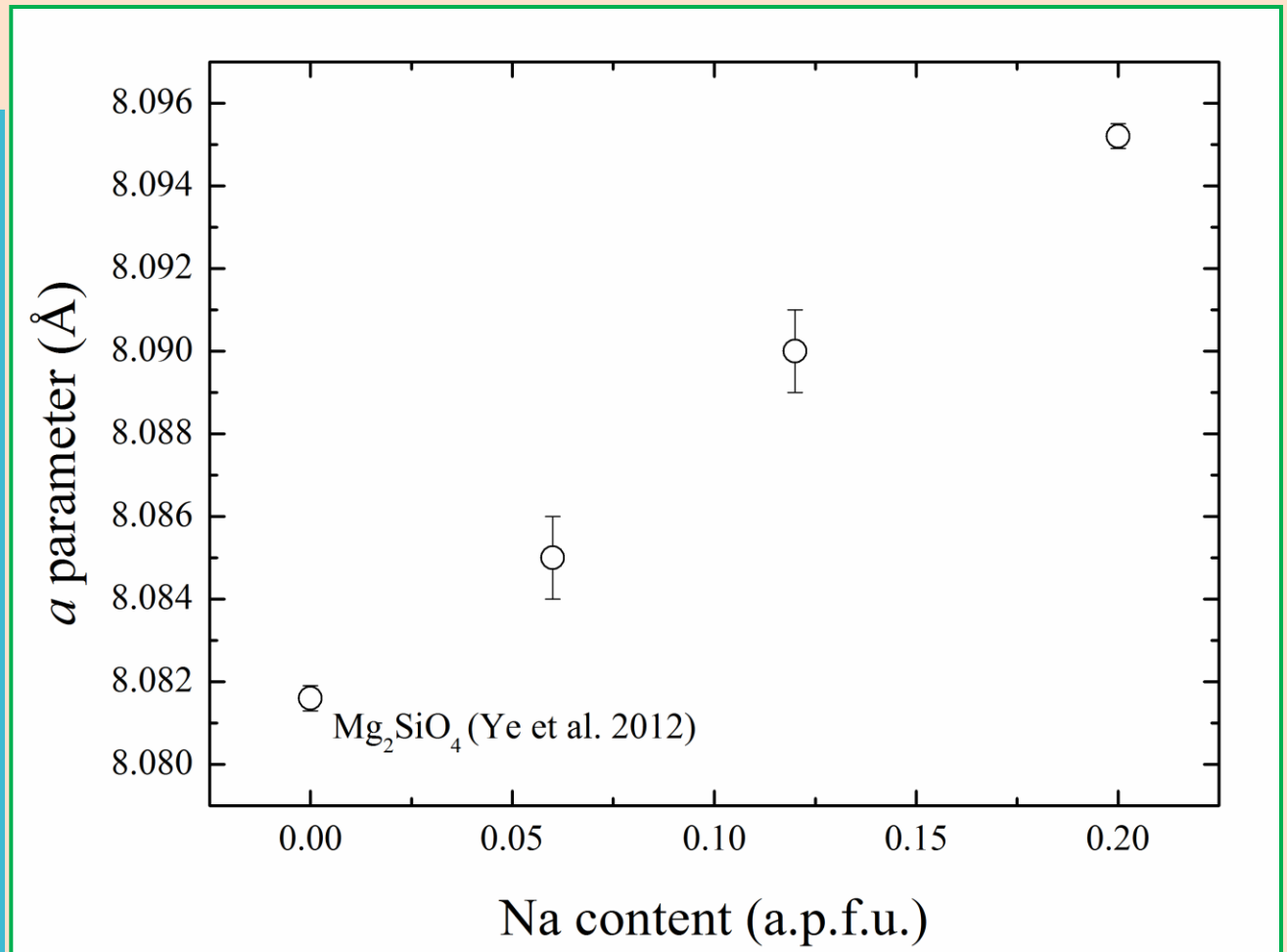
Mean octahedral bond distance = 2.088(1) Å (pure Mg<sub>2</sub>SiO<sub>4</sub> = 2.072 Å; Ye et al. 2012). On the basis of the reaction Mg<sup>2+</sup> → 2/3Na<sup>+</sup> + 1/3Si<sup>4+</sup>, substitution of twice the amount of Na with respect to Si results in an increase of the octahedral volume [12.01 Å<sup>3</sup> in Na-rgw1, 11.81 Å<sup>3</sup> in pure Mg<sub>2</sub>SiO<sub>4</sub>]

Does the incorporation of Na induce a distortion of the overall sublattice?



Such deviation of  $u$  indicates sublattice disorder through local deviation of cations (M-site) from  $16d$ . This provides a plausible explanation for the observed Na incorporation.  $16d$  sites with Na and Si are indeed more distorted ( $\sigma^2 = 12.21$ ) than pure Mg sites ( $\sigma^2 = 8.17$ ; Ye et al. 2012), yet there is no net deviation for the overall structure.

Is it possible to model the entry of Na in the ringwoodite structure?



$$a \text{ (Å)} = 8.0815(1) + 0.068(1) * \text{Na (a.p.f.u.)}$$

$$(R^2 = 0.999)$$

What about Na-bearing bridgmanite?

Can we apply the same crystal-chemical remarks for this phase?

Na-brg1 and Na-brg2:



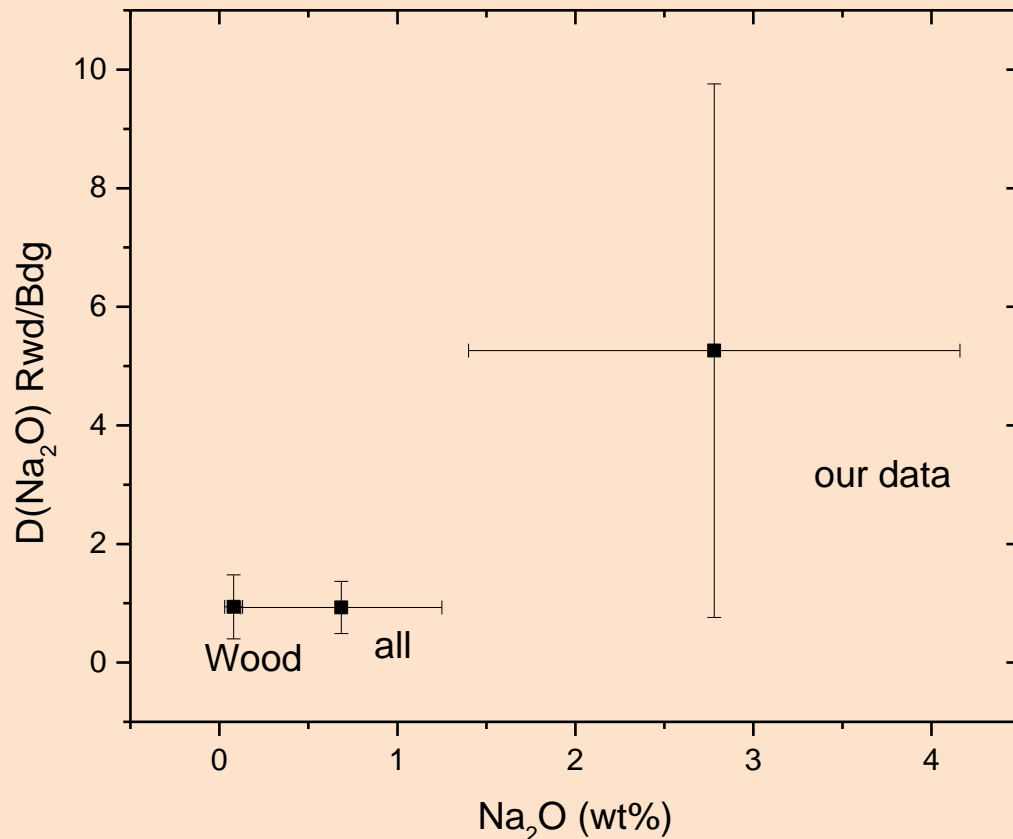
Not suitable single crystals were found

Unit-cell volume =  $166(1) \text{ \AA}^3$  is larger than that observed for pure  $\text{MgSiO}_3 = 162.53(1) \text{ \AA}^3$  (Dobson and Jacobsen 2004)

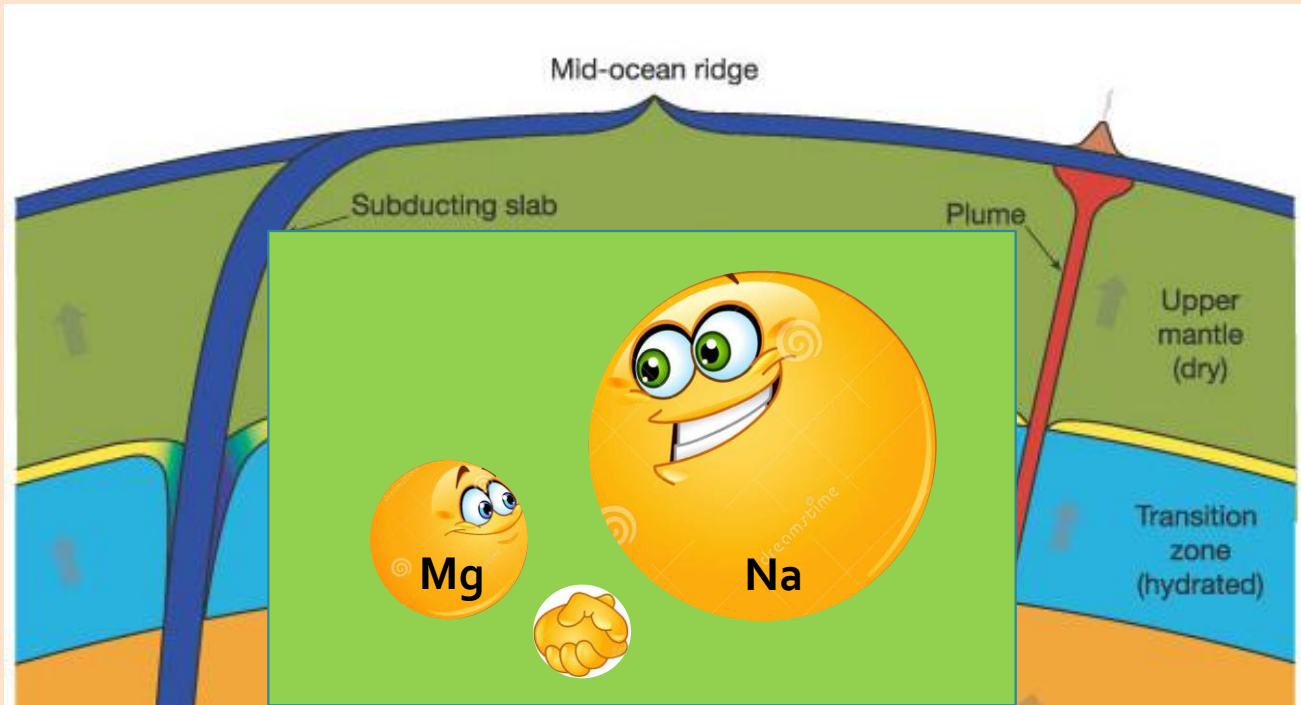
However, the mechanisms of Na incorporation in this structure remain unknown. The chemical compositions are not charge balanced: Na replaces Mg and Al replaces Si giving rise to an undercharged chemical formula (when the data are normalized to 3 oxygen atoms). A possible solution could be a partial oxygen vacancy, as commonly observed in O-deficient perovskites, but these considerations must await the availability of suitable single crystals for careful X-ray investigations.

$\text{Na}_2\text{O}$  is compatible in Rgw relative to Bdg with a partition coefficient (D) of 5 (+5/-4), **but is incompatible in Rgw relative to carbonate rich melt/fluid**, with the D value ranging between 0.5 and 0.1. Al is highly enriched in bridgmanite (same feature observed by Kato et al. 2014; PEPI, **232**, 26-29).

Some  
implication  
for the  
transport of  
alkali in the  
deep mantle?



The relatively high partition coefficient suggests that under certain conditions ringwoodite could act as an important host for Na, and perhaps K, in the deep transition zone.

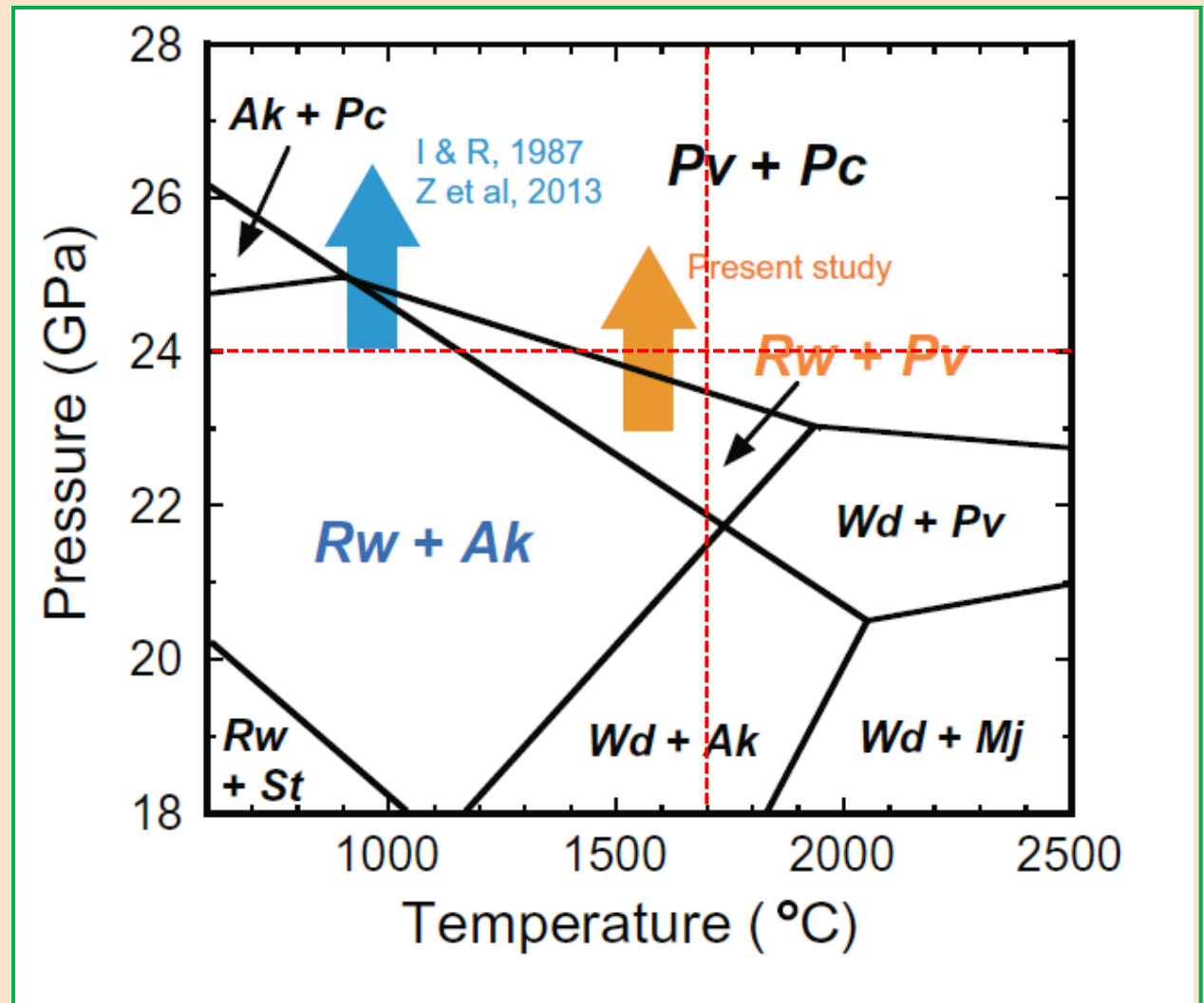


Carbonatitic melt metasomatism in the deep transition zone may lead to local Na-enrichment, and ringwoodite may be an important host for Na in the deep transition zone. Subsequent convection or subduction of metasomatised mantle may lead to enrichment of alkaline elements in the upper and lower mantle.

Some implication for the transport of alkali in the deep mantle?



Pressure and temperature and relationships among the different phases



Graph from Kato et al. 2014 (PEPI, **232**, 26-29)

Symbols: Mj = majorite; Ak = akimotoite; Pv = perovskite; Wd = wadsleyite; Rw = ringwoodite; Pc = periclase

## Main conclusions

- 1) The structural analysis of Na-rgw proved that the ringwoodite structure can host large amount of Na at the octahedral site
- 2) Na can enter the octahedral site of the spinel provided some smaller cations (i.e., Si) are present so as to reduce the average cation size (MOB model)
- 3) The entry of Na induces a distortion in the overall sublattice with a local deviation of cations from their  $16d$  position
- 4) The effect of Na incorporation in the spinel structure can be modeled with a simple linear regression
- 5) The mechanisms for Na incorporation in the bridgmanite structure remain unknown and await the availability of suitable single crystals.
- 6) Ringwoodite can be an efficient host for Na in the transition zone and play an important role for the transport of alkali in the lower mantle

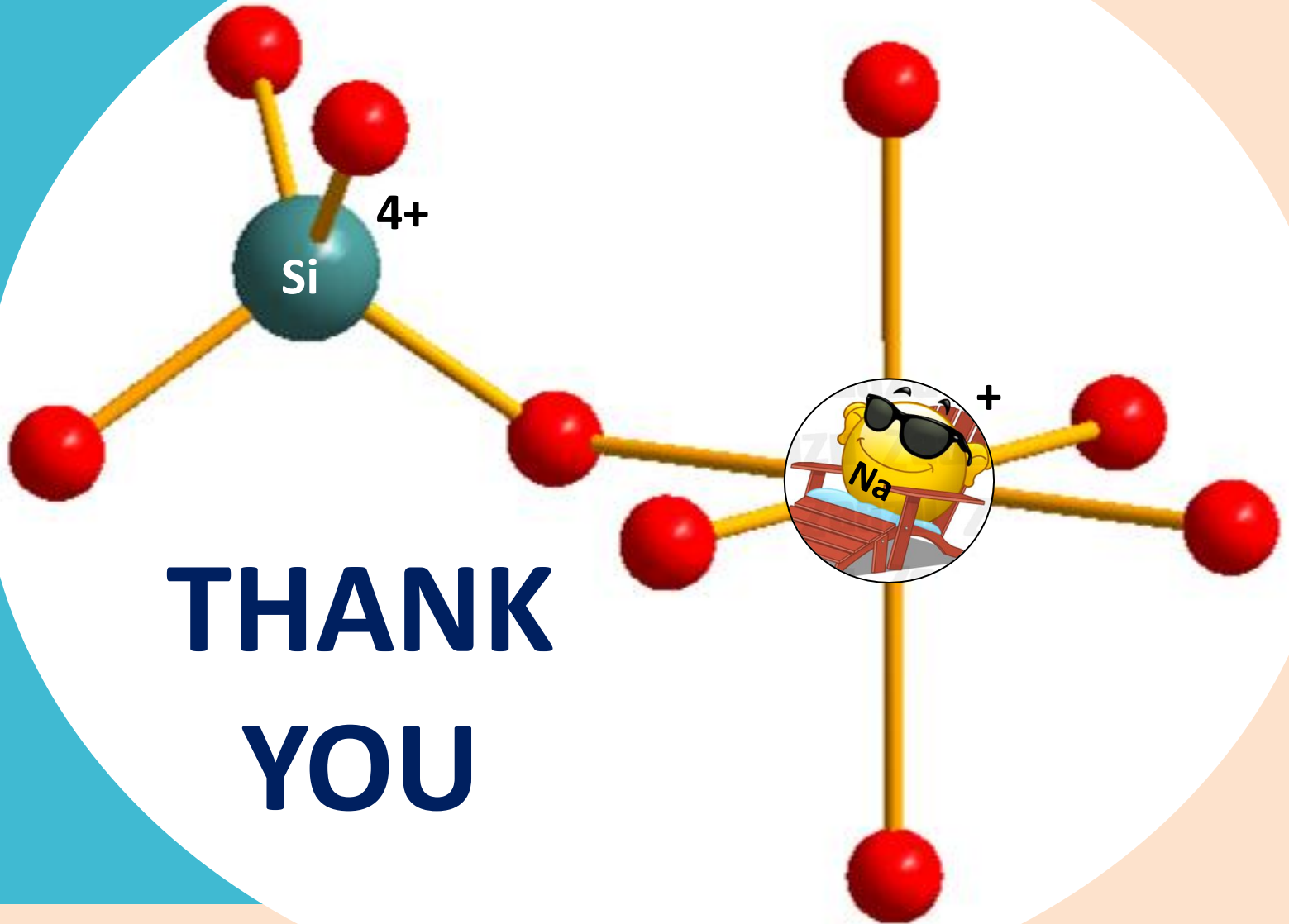
## Special thanks to...

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**THANK  
YOU**