Fluorine, Cl, Br and I in Serpentinites

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Introduction

Subduction at convergent plate boundaries provides a mechanism for recycling fluid-mobile elements from surface reservoirs into the Earth's mantle, and back again. Serpentinites are important in subduction zones because they contain up to 13 wt% H_2O and are stable to depths >100km [1], making them effective vehicles for the transport of volatile elements, such as halogens, into the mantle.

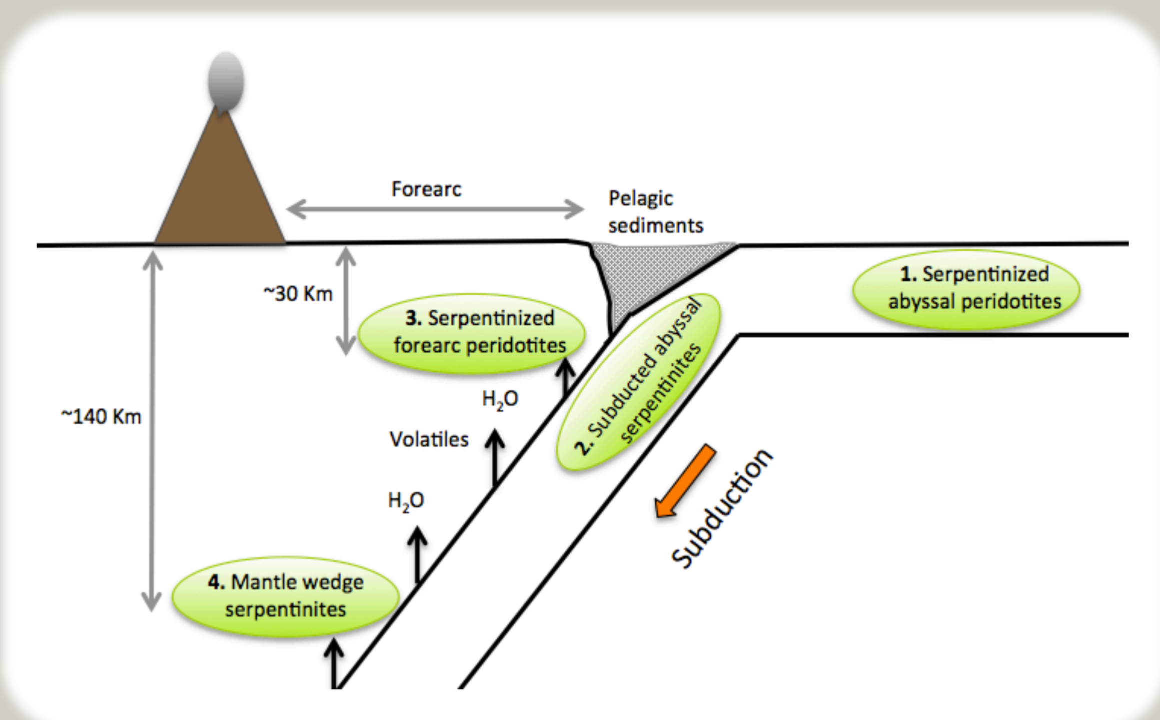
Most serpentinites are formed by hydration of abyssal peridotites on the ocean floor and near oceanic ridges [2]. They can also be formed along the outer rise of a subducting plate from fluid infiltration of faults in the bending slab [3]. Others originate from hydration of forearc mantle peridotites at the base of the mantle wedge by fluids released from the subducting slab [2].

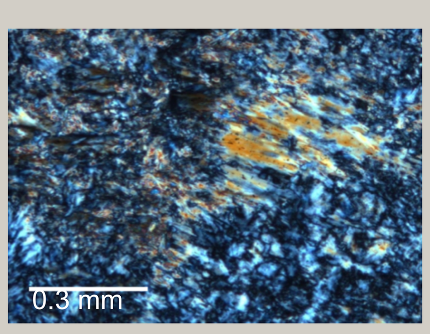
Halogen concentrations and derived ratios may be useful for interpreting fluid origin and mobility in shallow and deep subduction cycles. We investigate the behaviour of F, Cl, Br and I in subduction zones by analyzing serpentinites from four different origins.

Northern Dominican Republic:
1. Obducted hydrated abyssal peridotites
2. Subducted abyssal peridotites (~30km)
3. Shallow forearc mantle serpentinites (<30km)

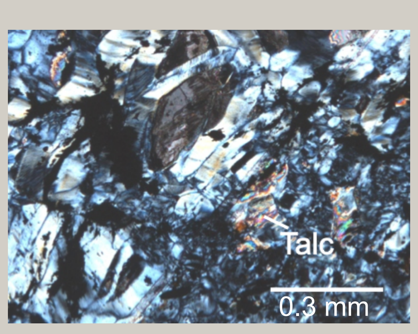
Northwest Himalayas:

4. Deep mantle wedge serpentinites (+ secondary olivine) (~140km)





RD91: shallowly subducted abyssal antigorite



RD34c: shallow forearc lizardite at base of mantle wedge

Methods

Halogen Extraction via Pyrohydrolysis

- I-125 tracer to evaluate chemical yield of set-up [4]
- 0.5 g washed & crushed sample + 0.5 g V_2O_5 accelerator in SiO_2 boat
- 0/8 $Lmin^{-1}$ wet O_2 flow
- 1100°C furnace temp.
- >120°C SiO_2 tube temp. outside furnace (heating tape)
- 30 min collection time
- Fritted glass tip submerged in 7 mL 25 mM NaOH trap solution
- Ice bath around trap to promote halogen dissolution

Halogen Analysis

- F and Cl: DIONEX ICS-2100 Ion Chromatography system with LOD (3σ) of 0.053 ppm (F) and 0.042 ppm (Cl)
- Br and I: Agilent Technologies 7700 series ICP-MS with LOD (3σ) of 0.028 ppb (Br) and 0.137 ppb (I)
- 10 samples analyzed for F + Cl by NaOH fusion, followed by IC, yielded similar results to pyrohydrolysis

References

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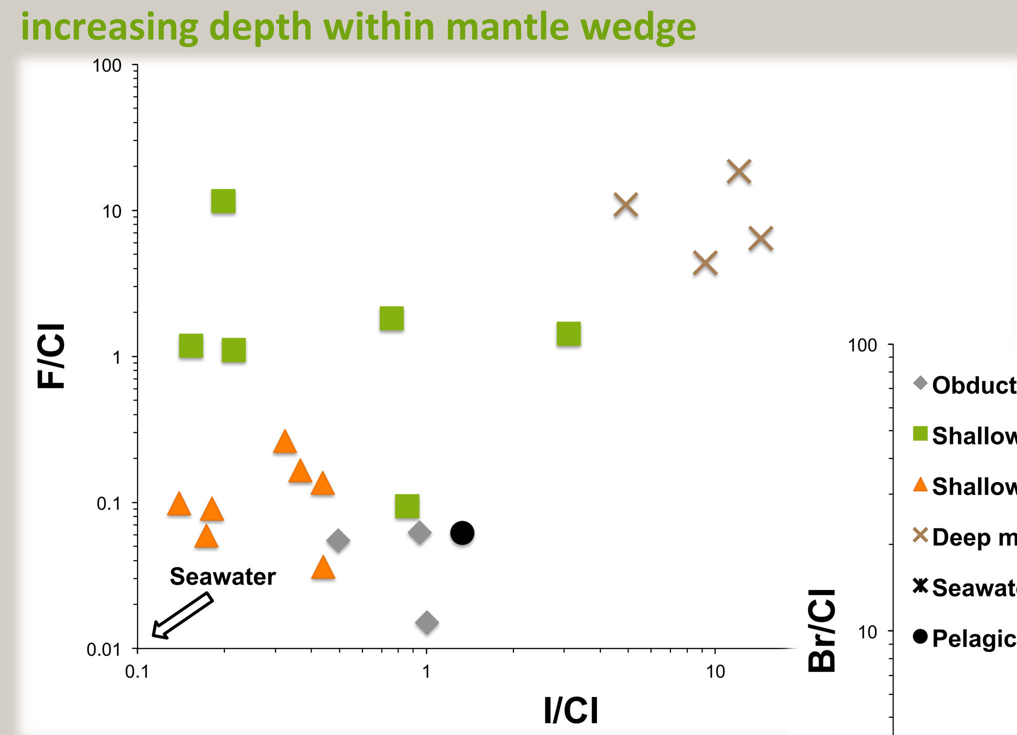
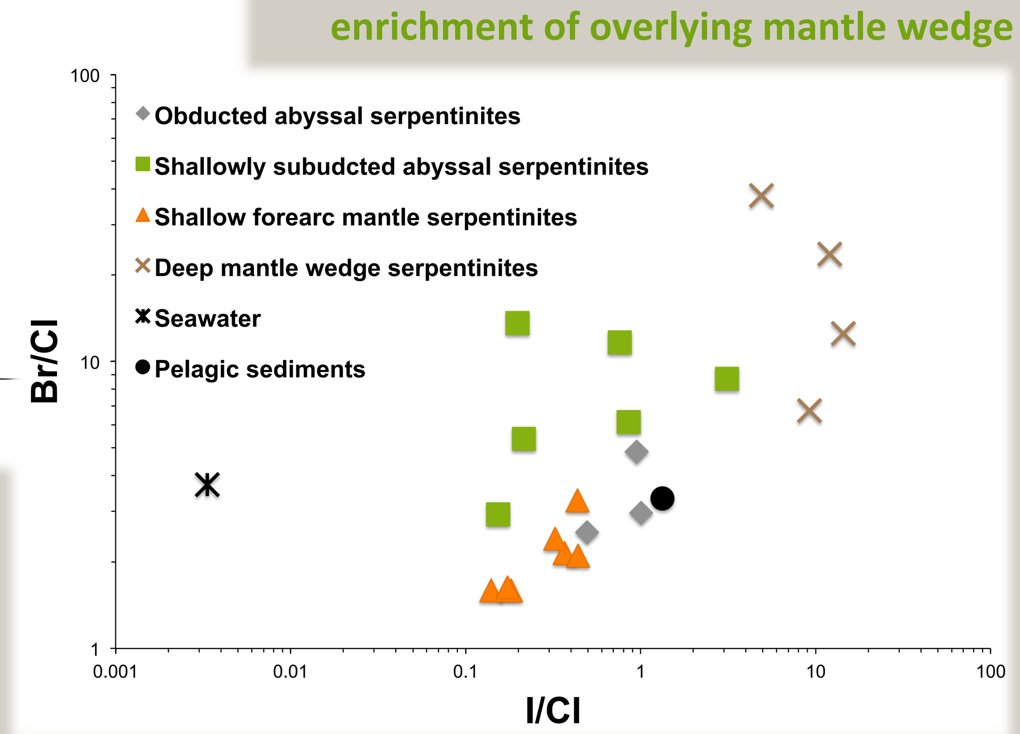
Results

Location	Protolith	Sample	Phase	F ppm	Cl ppm	Br ppm	I ppm	F/Cl	Br/Cl (x 10-3)	I/Cl (x 10-3)
Dominican Republic	Abyssal peridotite	*Obducted* Mean (n=3)	lizardite	13	340	1.0	0.3	0.044	3.5	0.8
		Shallowly subudcted Mean (n=6)	lizardite/ antigorite	72	52	0.30	0.031	2.9	8.1	0.9
	Forearc peridotite at base of mantle wedge	*Shallow* Mean (n=7)	lizardite	58	514	1.0	0.14	0.12	2.1	0.29
Himalayas		*Deep* Mean (n=4)	antigorite	149	18	0.30	0.18	10	20	10
---	---	Seawater [5]	---	1.3	18,000	67	0.06	0.00007	3.7	0.0033
---	---	Pelagic sediments [5]	---	1300	21,000	70	28	0.062	3.3	1.33

F/Cl vs. I/Cl ratios showing enrichment of F during seafloor subduction and increasing depth within mantle wedge



Br/Cl vs. I/Cl ratios showing depletion of Br and I during seafloor subduction and enrichment of overlying mantle wedge



Chlorine

- High in abyssal serpentinites from seawater hydration, but loss during subduction
- Elevated levels in shallow forearc samples suggest transfer of Cl from subducting slab to overlying mantle wedge
- Low values in base mantle wedge at depth indicates i) lack of Cl released from deeply subducted slab or ii) loss of Cl with increasing depth, possibly due to lizardite to antigorite phase transition

Bromine

- Mimics chlorine's behavior
- Elevated Br/Cl ratios in subducted abyssal and deep mantle wedge serpentinites suggest Br isn't as readily lost as Cl with increasing depth or possible phase transition

Iodine

- I/Cl ratios of seafloor serpentinites 240x seawater, consistent with literature [6]
- During shallow subduction I is released from slab and incorporated into shallow forearc peridotites
- Deep and shallow mantle wedge serpentinites contain similar I content, indicating retention with increasing depth

Fluorine

- F-enrichment of abyssal peridotites occurs during serpentinization at outer rise of bending slab by infiltration of fluids that were chemically altered by pelagic sediments
- Similar F content seen in shallow forearc serpentinite
- Further enrichment in deep mantle wedge by ascending slab-released fluids concentrated as water is consumed by hydration of peridotites
- Higher values in antigorite (+ secondary olivine) suggest F is concentrated during phase transition and serpentinite dehydration, agreeing with previous study [7]

Conclusions

- Forearc mantle peridotites are serpentinized by release of Cl-, Br- and I-rich fluids from subducting slab, whilst F is retained during subduction
- Cl and Br may be expelled during lizardite to antigorite phase transition, resulting in shallow cycles in subduction zones
- F and I are retained with increasing depth, suggesting serpentinites contribute to the transfer of these halogens into the deep mantle