F and Cl solubilities in wadsleyite and ringwoodite

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The relative distribution of volatile elements (e.g. H, C, F, Cl, S) in the different Earth's various reservoirs provides strong constraints on the understanding of the Earth's history. This study aims to access the mechanism and proportion of halogens that may be accomodated in minerals of Earth's Transition Zone (TZ; 410 to 660 km depth). The storage of water in the TZ is thought to be important due to its high solubility (up to 3.3 wt% water [1,2]) in wadsleyite (Wd) and ringwoodite (Rw), the two main phases of the TZ (60 % of its volume). As the halogen and water cycle are often linked (see the review after [3]), we investigate whether the TZ could be a deep reservoir for F and Cl. Therefore, we are measuring the F and Cl solubilities in Wd and Rw. F and Cl doped Wd and Rw samples were synthesized in multi-anvil press to reach the conditions of pressure and temperature of the TZ (14 to 22 GPa; 1100 to 1450°C). The obtained crystal sizes were greater than 10 μm, allowing precise mesurement of halogen contents in individual crystals. The synthesis were performed under both anhydrous and hydrous conditions to study the influence of water on the F and Cl solubilities. F and Cl quantification was realized by ion beam analysis: we used μ-PIGE (μ-Particle Induced Gamma Ray Emission) for F; and μ-PIXE (μ-Particle Induced X-ray Emission) for Cl. We show that F and Cl can be incorporated in Wd and Rw in significant amounts. F solubility decreases with the presence of water. This suggests that F (possibly Cl) and water (OH) are accommodated on the same crystallographic sites in Wd and Rw. If we assume that the transition zone would store significant amounts of Cl and F, it means that (1) the TZ has been continuously supplied by Cl and F-bearing subduction materials, or (2) TZ is a hidden deep light halogen elements reservoir which never exchanges with the rest of the mantle.
In both cases, F and Cl bulk silicate Earth contents may have been underestimated. If confirmed, the Earth's accretion models may have to be revisited.

[1] Inoue *et al*, (1995) JGR 22, 117-120; [2] Bolfan-Casanova *et al*, (2000) *EPSL* **18**, 2 209-221; [3] Pyle and Mather, *Chem Geol* (2009), **263**, 1-4, 110-121.

Mass independent isotope fractionation in Ozone

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We propose that the average lifetime of an activated O_3* complex yielding ozone and formed by collisions involving distinguishable isotopes in the reaction $O + O_2$, is not equal to the average lifetime of the same complex but formed by collisions involving indistinguishable isotopes. We ascribe the mass independent isotopic fractionation factor η [1] to the average lifetime ratio of complexes formed by reactions involving dis- and indistinguishable isotopes.

Calculated average lifetimes of the O_3* complexes in a thermal gas were obtained by classical trajectories of collisions $O + O_2$, where all atoms have the same mass (16 amu). Simulations have been carried out in an ab-initio potential surface [2] of three oxygen atoms in a singlet ground state. We derive the mass-dependent fractionation as measured in laboratory experiments [3] by including differences in the zero-point energies of involved O_2 molecules. The numerical results account well for the measured isotopic fractionation in ozone [3, 4], as reported in the Table 1.

Reactions		Complex	ΔZPE	α(M.D.)	η	α(calc.)	α(mes.)	
16	17-18	16-17-18[(*)]	0	1.00	1.20	1.20	≡ 1.20	NR+R
16	17-17	16-17-17	11.79	1.13	1.20	1.36	1.23	NR+R
16	18-18	16-18-18	22.76	1.26	1.20	1.51	1.50	NR+R
17	16-16	17-16-16	-11,62	0.87	1.20	1.04	1.03	NR+R
17	18-18	17-18-18	10.80	1.12	1.20	1.35	1.31	NR+R
18	16-16	18-16-16	-22,10	0.75	1.20	0.90	0.92	NR+R
18	17-17	18-17-17	-10.64	0.88	1.20	1.05	1.03	NR+R
18	16-18	18-16-18	-22,76	0.74	1.28	0.95	0.92	I+R
16	16-18	16-16-18	22.10	1.25	1.28	1.60	1.45	I+R
16	18-16	16-18-16		1.00	1.00	1.00	1.08	I
17	17-17	17-17-17		1.00	1.00	1.00	1.02	I
18	18-18	18-18-18		1.00	1.00	1.00	1.03	I
18	16-18	18-16-18		1.00	1.00	1.00	1.04	I

Table 1: ΔZPE the difference in zero-point energies; α(MD) the calculated mass-dependent fractionation factor; α(calc.) the overall calculated isotopic fractionation factor: α(calc.) = η x α(MD) [1]; α(mes.) the measured isotopic fractionation factor as reported by [3]; last column: the type of reaction. R and NR for reactive and non reactive, I for Indistinguishable. The reference reaction is shown by a (*).

[1] Gao, Y. Q., Marcus, R.A., 2001. *Science*. **293**, 259–263. [2] Schinke, R., Fleurat-Lessart, P., 2004. *J. Chem. Phys.*, **121**, 5789. [3] Janssen, C., *et al*. 2001. *Phys. Chem. Chem. Phys.* **3**, 4718-4721. [4] Thiemens, M.H., Heidenreich III, J.E., 1983. *Science*. **219**, 1073–1075.