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Chlorine isotope mantle heterogeneity: Constraints from theoretical first-principles calculations

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ABSTRACT

The processes that caused the heterogeneity of δ^{37}Cl in the Earth's mantle are unclear. Here we report theoretical estimates of equilibrium chlorine isotope fractionation among common chlorine-bearing minerals, namely apatite-group minerals (Cl-Ap, F-Cl-Ap, OH-Cl-Ap), muscovite, phlogopite, tremolite, lizardite, marialite and metal halides, based on first-principles calculations, and use them to provide an explanation for this heterogeneity. Our results show that at ambient P-T conditions, the reduced isotopic partition function ratio (β-factor) is strongly correlated with the metal-Cl bond length/bond strength of the above minerals and that phlogopite and muscovite are more enriched in ^{37}Cl than other minerals. As a result of a number of factors, including the adjacent atomic environment, the sites occupied by chlorine atoms in crystals, the Cl-metal coordination and the crystal density, the sensitivity of $10^3\ln\beta$ to pressure follows the sequence: halite > fluoro-chlorapatite > chlorapatite > marialite > hydroxyl-chlorapatite > lizardite > tremolite > muscovite > phlogopite. Estimates of the chlorine isotope fractionation between metamorphic minerals and aqueous fluid at the pressure and temperature prevailing during subduction indicate that the δ^{37}Cl values of mantle minerals could vary between -6‰ and +3‰, assuming equilibrium. In contrast, the average δ^{37}Cl value of the bulk mantle is -0.53±0.16‰. Thus, large-scale recycling of volatile Cl from the deep mantle to the continental/oceanic crust and ocean, and the isotopic fractionation of chlorine with increasing metamorphic grade during subduction, could explain the heterogeneity of δ^{37}Cl values observed in mantle materials.

Keywords: Equilibrium chlorine isotope fractionation; chlorine-bearing minerals; P-T-dependent reduced isotopic partition function ratios (β-factor); chlorine isotope mantle heterogeneity

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1. Introduction

Chlorine is a volatile and strongly hydrophilic element (Sharp et al., 2010) that has two stable isotopes, ^{35}Cl with 18 neutrons and ^{37}Cl with 20 neutrons. The relative natural abundances of these isotopes are 75.76% and 24.24%, respectively (Berglund and Wieser, 2011). With average concentrations of 30 ppm in the primitive mantle and 244 ppm in the continental crust, chlorine is the most abundant of the halogen group of elements (Palme and O'Neill, 2014; Rudnick and Gao, 2003). It reaches its highest concentration, however, in water. For example, seawater contains 1.9 wt% Cl and the chlorine content of aqueous fluids exsolving from silicate magmas can exceed 10 wt% as a result of the strong preference of chlorine for the aqueous phase (Barnes and Sharp, 2017). This has led to the suggestion that the main hosts of chlorine in the Earth's mantle are fluid inclusions and the OH site in hydrous minerals (e.g., amphibole, mica and apatite) (Luth, 2014).

The various terrestrial chlorine reservoirs have δ^{37}Cl values that range collectively from -14‰ to +16‰ (Kaufmann et al., 1984; Volpe et al., 1994; Eggenkamp et al., 1995; Willmore et al., 2002; Godon et al., 2004). Most δ^{37}Cl values are close to 0‰. For example, in evaporites, they vary from -0.5‰ to +0.8‰ (Eastoe et al., 2001; Eggenkamp et al., 2019ab). Serpentine group minerals have been a particular focus of previous chlorine isotope studies because of the importance of serpentinites in the global chlorine cycle (e.g., Anselmi et al., 2000; Barnes and Sharp, 2006; Bonifacie et al., 2008). The chlorine isotopic composition of serpentinites and related ultramafic rocks has been analyzed for the same reason. Thus, Bonifacie et al. (2008) determined the bulk-rock chlorine content and isotopic composition (δ^{37}Cl) of oceanic serpentinites, high-pressure metaperidotites and associated metasedimentary rocks in order to constrain the contribution of hydrothermal alteration and subduction of oceanic lithosphere to the chlorine content of the mantle and, more broadly, the global chlorine cycle. Much of our information on the chlorine isotopic composition of the mantle comes from the study of mid-ocean ridge basalts (MORBs), which can have relatively wide ranges in δ^{37}Cl values as shown in Figure 1. Indeed, Stewart et al. (1998) concluded that enriched mantle reservoirs with a recycled crustal component are depleted in ^{37}Cl relative to the Standard Mean Oceanic Crust (SMOC), whereas the un-degassed mantle is enriched in ^{37}Cl relative to SMOC. This conclusion is supported by the finding of Bonifacie et al. (2007, 2008) that the mantle source for MORB (degassed) has a δ^{37}Cl value $\leq$ -1.6‰. In contrast, analyses of samples representing the subcontinental mantle have yielded δ^{37}Cl values of 0.01 ± 0.25‰ (Sharp et al., 2007). Contrary to conclusions reached about the chlorine isotopic composition of the mantle based on studies of MORB, those based on Ocean Island Basalts (OIB) record positive values. Thus, John et al. (2010) showed that HIMU-type mantle has δ^{37}Cl values ranging from -1.6 to +1.1‰, and EM-type mantle values ranging from -0.4 to +2.9‰. Finally, the δ^{37}Cl values of primary carbonatite, a rock-type representative of small degrees of partially melting of metasomatically altered mantle, vary from -0.8 to +0.1‰; the variation may be greater in some cases due to chlorine isotopic fractionation during post-emplacement evolution of the magma (Eggenkamp and Koster van Groos, 1997). Sharp et al. (2013) measured many additional mantle-derived phases and obtained a tight clustering of δ^{37}Cl values between -0.3‰ and -0.1‰. The inescapable conclusion of all these studies is that the chlorine isotopic composition of the mantle is extremely heterogeneous (Stewart and Spivack, 2004; Barnes and Sharp, 2017). A question that has not been resolved, however, is the cause(s) of this heterogeneity. One possibility is the subduction of crustal material (e.g., sediment), which some researchers have used to explain the strongly positive δ^{37}Cl values of EM-type mantle (e.g., John et al., 2010). Another possibility is mantle metasomatism, which Sharp et al. (2007) has used to explain the distinctly lower δ^{37}Cl values (-1‰) of MORB glasses from the East Pacific Rise.

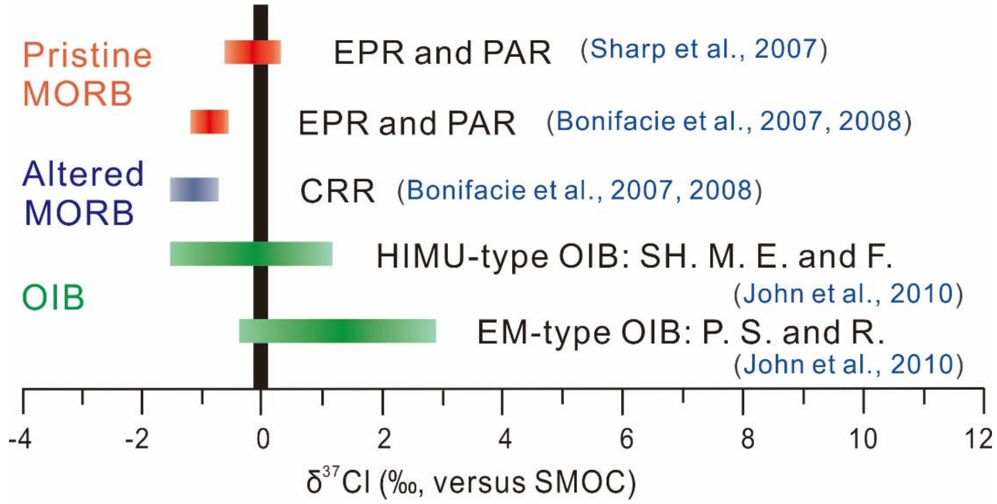

Figure 1. Chlorine isotope variability in mantle-derived materials (Bonifacie et al. 2007, 2008; Sharp et al., 2007; John et al., 2010). EPR: East Pacific Rise; PAR: Pacific Antarctic Ridge; CRR: Costa Rica Rift; SH: St. Helena; M.: McDonald; E.: Easter; F.: Foundation; P.: Pitcairn; S.: Societies; R.: Réunion.

The fractionation of chlorine isotopes by processes such as multiple evaporative cycles (Eggenkamp et al., 1995, 2016, 2019ab; Eastoe et al., 2001, 2016), diffusion and ion filtration (Eggenkamp et al., 1994, 2009; Beekman et al., 2011; Agrinier et al., 2019), and water-rock interaction (Barnes and Straub, 2010; Marques et al., 2020) has been well-documented. As a result, chlorine isotopes have found a variety of applications, including tracing the time-dependent processing of volatiles in subduction zones (e.g., Barnes et al., 2008; Barnes and Straub, 2010; Rizzo et al., 2013; Bernal et al., 2014; Chiaradia et al., 2014; Cullen et al., 2015; Li et al., 2015), differentiating fluid types and evaluating evolutionary processes of brine and pore water (e.g., Eggenkamp et al., 1995; Eastoe et al., 1999, 2001, 2016; Shouakar-Stash et al., 2007; Stotler et al., 2010; Alexeeva et al., 2015; Agrinier et al., 2019; Zhao et al., 2020), fingerprinting organic contaminant in hydrologic systems (e.g., Shouakar-Stash et al., 2003, 2006), unraveling chloride sources in soils of the Antarctic dry valleys (e.g., Bao et al., 2008) and constraining the sources of mineralizing fluids in ore deposits (e.g., Eastoe et al., 1989; Eastoe and Guilbert 1992; Bonifacie et al., 2005; Liebscher et al., 2006; Nahnybida et al., 2009; Gleeson and Smith, 2009; Richard et al., 2011; Hanley et al., 2011). The halogen contents and ratios are sensitive monitors for a variety of processes in magmatic-hydrothermal systems, including magmatic fractionation, volatile loss, and fluid-rock interaction (Eggenkamp et al., 2020). In addition to the above, it is essential to understand the processes responsible for the δ^{37}Cl heterogeneity of the mantle.

In recent years, considerable progress has been made in theoretically modeling the equilibrium fractionation of stable isotopes among different phases (Schauble, 2004; Schauble et al., 2009; Blanchard et al., 2017). Examples of this include oxygen and silicon isotope fractionation among silicate minerals (Méheut et al., 2007, 2009, 2014; Huang et al., 2014), magnesium and calcium isotope fractionation among aqueous Mg^{2+}, brucite, silicate, oxide and carbonate minerals (Schauble, 2011, Huang et al., 2013, 2019; Wang et al., 2019; Antonelli et al., 2019) and chlorine isotope fractionation among chlorine-bearing molecules, metal chlorides, silicate minerals, aqueous chloride-gas systems (Schauble et al., 2003; Czarnacki and Halas, 2012; Balan et al., 2019).

The pioneering theoretical study of Schauble et al. (2003) showed that equilibrium chlorine isotopic fractionation is controlled mainly by the oxidation state of Cl and its bonding partner, such that molecules with oxidized Cl concentrate ^{37}Cl relative to chloride, wheeas metal chlorides with higher cation electrovalence (e.g., $FeCl_2$, $MnCl_2$) enrich ^{37}Cl relative to those of with lower electrovalence like NaCl, KCl and RbCl (Schauble et al., 2003). This study was the first to estimate the reduced isotopic partition function (β factors) of hydrated Cl^-_{aq}, taking the interaction of the chloride ion with H_2O into account, and the first to calculate chlorine isotopic fractionation factors for Cl_2-HCl-Cl^- aqueous-gas systems (Czarnacki and Halas, 2012). A recent, first-principles, modeling of chlorine isotopic fractionation between Cl-bearing molecules and minerals at ambient pressure clearly documented the importance of the local bonding environment in controlling chlorine isotope fractionation (Balan et al., 2019). As chlorine is one of major volatiles recycled on a large-scale from the interior to the surface of Earth, measurements of its isotopic composition in earth materials provide a potentially powerful means of tracking the progress of processes like subduction that are important vehicles for this recycling. For such tracking to be possible, however, it is necessary to consider the effect of pressure on the isotopic fractionation of chlorine.

This paper reports the results of a study of chlorine isotopic fractionation for the major chlorine-bearing metamorphic minerals (i.e., apatite-group minerals, muscovite, phlogopite, tremolite, lizardite, marialite and metal halides) as a function of temperature and pressure. The main objective of the study was to quantify the extent of chlorine isotope fractionation among chlorine-bearing minerals in high-pressure (HP) and ultra-high pressure (UHP) environments, with the aim of assessing the factors controlling equilibrium chlorine isotope fractionation that might impact on the chlorine isotope heterogeneity of the mantle.

2. Calculation details

2.1. Mineral models

Common chlorine-bearing metamorphic minerals, namely apatite-group minerals (Cl-Ap, F-Cl-Ap, OH-Cl-Ap) ($Ca_5(PO_4)_3(F,Cl,OH)$), muscovite ($KAl_2(Si_3Al)O_{10}(OH)Cl$), phlogopite ($KMg_3(Si_3Al)O_{10}(OH)Cl$), tremolite ($Ca_2Mg_5Si_8O_{22}(OH)Cl$), lizardite ($Mg_3Si_2O_5(OH,Cl)_4$), marialite ($Na_4Al_3Si_9O_{24}Cl$) and metal halides (halite) (NaCl) are considered in this study. The mineral structures were built, based on the Material Studio Materials Visualizer module (Accelrys, Inc., version 7.0), with reference to the experimental lattice parameters from the American Mineralogist Crystal Structure Database (Downs and Hall-Wallace, 2003). The crystal structures of these minerals are illustrated in Figure 2 and the modeling parameters are listed in Table 1. The chlorine content of the minerals considered (i.e., wt.%) in our models, i.e., chlorapatite, fluoro-chlorapatite, hydroxyl-chlorapatite, muscovite, phlogopite, tremolite, lizardite, marialite and halite, was estimated to be 6.8%, 3.5%, 3.5%, 8.5%, 8.1%, 4.3%, 1.6-40.4%, 4.2% and 60.7%, respectively.

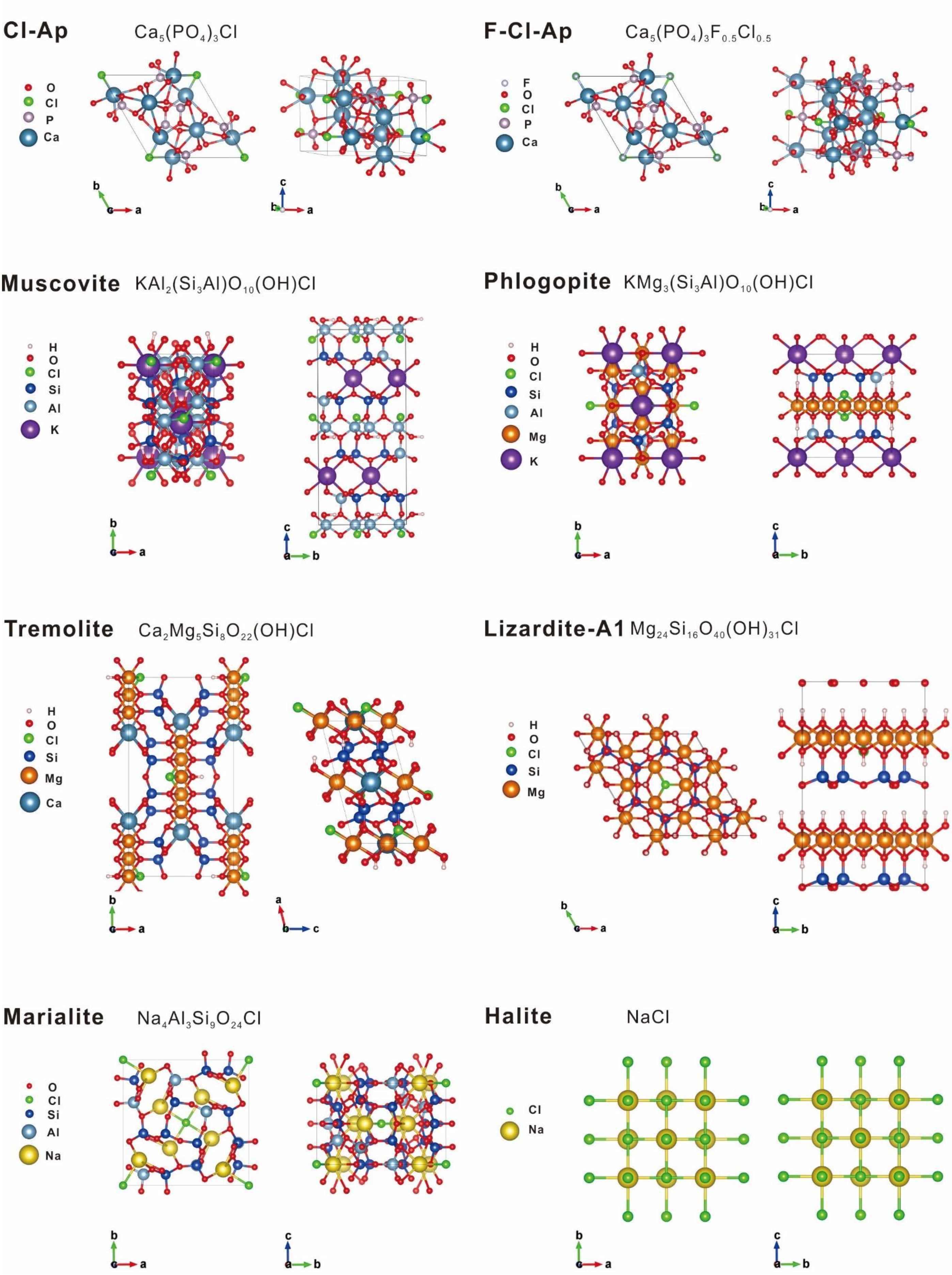

Figure 2. A series of periodic boundary cell (PBC) models for minerals, presented as top and side views.

2.2. Calculation methods

A simplified approximation for estimating mass-dependent equilibrium isotopic fractionation given by Bigeleisen and Mayer (1947) is suitable for most substances, assuming that there is rigid rotation and harmonic vibration. For a chlorine isotope exchange reaction, if there is only one chlorine atom in substance X and *n* chlorine atoms in substance Y, this exchange reaction is:

$$\mathrm{nX} + \mathrm{Y}^* \leftrightarrow \mathrm{nX}^* + \mathrm{Y} \qquad \text{(Eq. 1)}$$

where X and Y identify the substances containing the lighter isotope (^{35}Cl), X* and Y* identify the substances containing the heavier isotope (^{37}Cl) and *n* is the number of chlorine atoms (^{37}Cl) substituted in Y*.

The isotope fractionation factor (α) for the general isotope exchange reaction between X and Y can then be written as (Liu and Tossell, 2005):

$$\alpha = \frac{\mathrm{RPFR(X)}}{\mathrm{RPFR}^{\frac{1}{n}}\mathrm{(Y)}} = \frac{\beta(\mathrm{X})}{\beta(\mathrm{Y})} \qquad \text{(Eq. 2)}$$

The harmonic approximation for the reduced isotopic partition function ratio (RPFR, or β factor) of X and Y is given by Eq. 3 below (Bigeleisen and Mayer, 1947; Kieffer and Werner, 1982; Dove, 1993; Schauble, 2004; Kowalski et al., 2013; Wu et al., 2015; Young et al., 2015; Li et al., 2017).

$$\beta = \frac{Q^*}{Q} = \left[\prod_{i=1}^{3N_{at}} \prod_q \frac{u^*_{q,i}}{u_{q,i}} \frac{\exp\left(-\frac{u^*_{q,i}}{2}\right)}{1-\exp\left(u^*_{q,i}\right)} \frac{1-\exp\left(u^*_{q,i}\right)}{\exp\left(-\frac{u^*_{q,i}}{2}\right)}\right]^{1/N_qN} \qquad \text{(Eq. 3)}$$

where Q is the vibrational partition function, the asterisk refers to the heavy isotope, subscript *i* is the number of vibrational modes and N_{at}, N_q, and N represent the number of atoms in a unit cell, phonon wave vectors, and sites of isotopes, respectively (Schauble et al., 2006; Blanchard et al., 2009; Li et al., 2017). The term $u_{q,i}$ ($u^*_{q,i}$) can be calculated using Eq. 4:

$$u_{q,i} = \frac{hc \cdot \upsilon_{q,i}}{kT} \qquad \text{(Eq. 4)}$$

where *h* is Plank's constant, *c* is the speed of light, $\upsilon_{q,i}$ is a harmonic vibrational frequency of the *i*th vibrational mode at a phonon wave vector *q*, *k* is Boltzmann's constant and *T* is temperature in degrees Kelvin.

The term β is a function of the unit cell volume, pressure and temperature, and can be expressed as a function of *P* and *T* in combination with the equation of state of $P(V,T) = \partial F(V,T)/\partial V$ (Huang et al., 2013; Wu et al., 2015). The quasi-harmonic approximation for the Helmholtz free energy, *F*(*V*, *T*), is given by:

$$F(V,T) = U(V) + \sum_{qj} \frac{hw_{qj(V)}}{2} + K_B T \sum_{qj} \ln(1 - \exp[\frac{hw_{qj(V)}}{K_B}]) \qquad \text{(Eq. 5)}$$

where *q* is a wave vector in the first Brillouin zone, *j* is an index of the phonon mode with frequency ω_{qj}, and *V* and *T* are the volume and temperature of the system, respectively. The first, second, and third terms in Eq. 5 are the static internal, zero-point, and vibrational energy contributions, respectively. The relationships between the Helmholtz free energy and volume are expressed in terms of (or approximated by) the third-order Birch-Murnaghan finite-strain equations of state (Huang et al., 2013).

The Brillouin zone (BZ) was sampled with variable k-point preferentially following a rule of *a*×k1≈*b*×k2≈*c*×k3 for geometry optimization. The energy cut-off for the plane wave basis was from 830 to 990 eV. The generalized-gradient approximation (GGA) method together with the exchange-correlation functional of Perdew, Burke and Ernzerhof (PBE) (Perdew et al., 1996), and norm-conserving pseudopotentials were employed in both geometric optimizations and phonon calculations for the PBC model of the chlorine-bearing minerals. The computation details for supercell size, total atoms per cell, cut-off energy, k-points, q-points and quality set are listed in Table 1. The calculations were carried out using the Cambridge Serial Total Energy Package (CASTEP) (Clark et al., 2005).

Table 1. Calculation sets for chlorine-bearing minerals

Minerals	Formula	Supercell	N_{atoms}	Cut-off energy (eV)	k-points	q-points	Quality
Chlorapatite	$Ca_5(PO_4)_3Cl$	1×1×1	42	880	2×2×2	4	Ultra-fine
		1×1×2	84	880	2×2×1	4	Ultra-fine
Fluoro-chlorapatite	$Ca_5(PO_4)_3F_{0.5}Cl_{0.5}$	1×1×1	42	940	2×2×2	4	Ultra-fine

Hydroxyl-chlorapatite	$Ca_5(PO_4)_3(OH_{1-x}Cl_x)$						
	$Ca_5(PO_4)_3(OH_{0.5}Cl_{0.5})$	1×1×1	43	880	2×2×2	4	Ultra-fine
	$Ca_5(PO_4)_3(OH_{0.75}Cl_{0.25})$	1×1×2	87	880	2×2×2	2	Ultra-fine
	$Ca_5(PO_4)_3(OH_{0.5}Cl_{0.5})$	1×1×2	86	880	2×2×1	4	Ultra-fine
	$Ca_5(PO_4)_3(OH_{0.25}Cl_{0.75})$	1×1×2	85	880	2×2×2	2	Ultra-fine
Muscovite	$KAl_2(Si_3Al)O_{10}(OH)Cl$	1×1×1	80	830	3×2×1	6	Ultra-fine
Phlogopite	$KMg_3(Si_3Al)O_{10}(OH)Cl$	1×1×1	42	990	3×2×1	12	Ultra-fine
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)Cl$	1×1×1	80	990	1×1×3	6	Ultra-fine
Lizardite-A0	$Mg_3Si_2O_5Cl_4$	1×1×1	14	990	3×3×2	8	Ultra-fine
Lizardite-A1	$Mg_{24}Si_{16}O_{40}(OH)_{31}Cl$	1×1×1	143	990	2×2×1	1	Ultra-fine
Lizardite-A2	$Mg_{24}Si_{16}O_{40}(OH)_{31}Cl$	1×1×1	143	990	2×2×1	1	Ultra-fine
Lizardite-A3	$Mg_{24}Si_{16}O_{40}(OH)_{30}Cl_2$	1×1×1	142	990	2×2×1	1	Ultra-fine
Marialite	$Na_4Al_3Si_9O_{24}Cl$	1×1×1	82	830	1×1×2	8	Ultra-fine
Halite	NaCl	1×1×1	8	830	3×3×3	36	Ultra-fine

Note: ‘Quality’ is a data quality control tab and used to limit parameter sets, such as K-points, Cut-off energy, and q-points. Generally, ‘Ultra fine’ means the most accurate results at the expense of the longest calculation time provided by CASTEP.

K-points: used for Brillouin zone sampling; the magnitude of the error in the total energy can be reduced by using a denser set of k-points.

Cut-off energy: the periodic system (mineral model) is calculated with plane wave basis sets; a higher cut-off energy corresponds to the use of more plane waves to describe the system.

q-points: used in the real space dynamical matrix calculations to obtain a set of frequencies at each point.

2.3. Pressure ranges in the mineral computational setting

Apatite, which can be described by the general formula $A_5(XO_4)_3Z$, is a versatile mineral that can incorporate a diverse range of major and trace elements, including the halogens, in its structure and is stable over a wide range of P-T conditions (up to 7.5 GPa in subduction zones) (e.g., Pan and Fleet, 2002; Hughes and Rakovan, 2015; Andersson et al., 2019). The A-site accommodates large cations (e.g., Ca^{2+}, Sr^{2+}, Pb^{2+}, Ba^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+}, REE^{3+}, Eu^{2+}, Cd^{2+}, Na^{+}), and the X-site is occupied primarily by P^{5+} (as PO_4^{3+}), which is in IV-fold coordination. This site can also accommodate other small, highly-charged cations (e.g., Si^{4+}, S^{6+}, As^{5+}, V^{5+}). The Z site is occupied by the halogens F^- and Cl^-, as well as by OH^-. The stability of apatite varies depending on the pressure and temperature. At 950 °C and a pressure of 7.5 GPa, OH-apatite breaks down to tuite {γ-$Ca_3(PO_4)_2$} (Konzett and Frost, 2009). This pressure limit on its stability, however, increases with increasing temperature and between 1100 and 1300 °C, OH-apatite is stable up to a pressure of 12 GPa; the corresponding temperature for F-apatite is between 1300 and 1500 °C (Murayama et al., 1986). Consistent with these constraints, we have assessed the effect of pressure on the fractionation of chlorine isotopes between apatite and other phases for pressures from 0 to 10 GPa.

The effect of high pressure on the fractionation of chlorine isotopes between micas and other phases is of interest because micas are considered to be the main repository of water and alkali metals in the mantle, and therefore play a critical role in the genesis of magmas above subduction zones (e.g., Schmidt et al., 2004). Phlogopite has three octahedral cations that coordinate with the hydroxyl anion, and muscovite has two octahedral cations and a vacancy. The different coordination environments lead to differences in the vibrational response of the hydroxyl ion. The chlorine isotopic fractionation of muscovite {$KAl_2(Si_3Al)O_{10}(OH)Cl$} and phlogopite {$KMg_3(Si_3Al)O_{10}(OH)Cl$} was investigated for 0, 0.05, 0.5, 2.5 and 5.0 GPa, pressures that span the range for subducting crust.

Amphiboles show great compositional variability and are stable over a wide range of P-T conditions from those of the crust to the upper mantle (e.g., Green and Wallace, 1988; Comodi et al., 1991). Tremolite {$Ca_2Mg_5Si_8O_{22}(OH)Cl$} is a low-pressure amphibole, with silicon in tetrahedral coordination and only magnesium in octahedral coordination (Comodi et al., 1991). It can form as a result of a reaction involving dolomite, quartz and water that also produces calcite and carbon dioxide (Skippen, 1971). Kirby (1987) investigated the stability of polycrystalline tremolite by constructing a phase diagram corresponding to the bulk composition of tremolite and showed that tremolite is stable up to a pressure of ~ 2.5 GPa. The pressure dependence of chlorine isotopic fractionation in tremolite was investigated for 0, 0.05, 0.5, 1.0 and 2.5 GPa.

Scapolite is a framework aluminosilicate of tetragonal symmetry that is stable over a wide range of P-T conditions and is observed mainly in metamorphic rocks (Baker and Newton, 1994). The generalized chemical formula for scapolite is $M_4[T_{12}O_{24}]A$, where M = Na and/or Ca, T = Si or Al, and A = Cl^- and/or CO_3^{2-}. The scapolite group comprises two members, marialite {$Na_4Al_3Si_9O_{24}Cl$; Ma} and meionite {$Ca_4Al_6Si_6O_{24}CO_3$; Me}, which form a continuous solid solution series. Most reports of marialite have been of occurrences in greenschist to eclogite facies, and in contact and retrograde metamorphic assemblages (Kullerud and Erambert 1999; Bernal et al., 2017; Lotti et al., 2018). Marialite of hydrothermal origin has been reported from a number of ore deposits (Almeida and Jenkins, 2017). In order to avoid the issue of the tetragonal-to-triclinic phase transition, which takes place at ca. 9.5 GPa (Lotti et al., 2018), chlorine isotope fractionation involving scapolite was investigated for pressures of 0, 0.05, 0.5, 2.5 and 5.0 GPa.

At ambient P-T conditions, halite crystallizes in the so-called rock salt structure, a cubic array of Na and Cl atoms in equal proportions (1:1 stoichiometry) with six-fold coordination. This structure is stable to relatively high pressure. A structural phase transition to the cubic, eight-fold coordinated NaCl-B2 phase is observed at ~30 GPa (Zhang et al., 2013). The chlorine isotope fractionation of halite was investigated over the pressure range from 0 to 10 GPa.

Serpentine {$Mg_3Si_2O_5(OH)_4$}, an alteration (hydration) product of olivine and pyroxene, is thought to be an important component of the descending slab (Ringwood, 1975; Gregory and Taylor, 1981; Meade and Jeanloz, 1991). Serpentine group minerals (e.g., lizardite, antigorite) are trioctahedral phyllosilicates, the structure of which is based on the stacking of a 1:1 layer composed of one octahedral and one tetrahedral sheet (Wicks and O'Hanley, 1988). Lizardite, the most abundant serpentine mineral in the Earth's upper crust, has the most straightforward structure, and is the standard for comparison in estimating the structures of the other serpentine group minerals (Dódony and Buseck, 2004). The powder X-Ray diffraction patterns from lizardite samples at high pressure and room temperature show that the crystal structure of serpentine is gradually eliminated by compression above 6.6 GPa (Meade and Jeanloz, 1990, 1991). In order to increase the database of thermodynamic properties of serpentine, Hilairet et al. (2006) determined the P-V Equations of State (EoS) of lizardite and chrysotile at ambient temperature up to 10 GPa, by in situ synchrotron X-Ray diffraction in a diamond-anvil cell. Neither amorphization or hysteresis was observed during compression and decompression, and no phase transition was resolved for lizardite. Experiments by Capitani and Stixrude (2012) failed to detect a tetrahedral bulk modulus for lizardite at pressures of 7-23 GPa, although an elastic anomaly was predicted to be present at about 6 GPa in a first-principles density functional calculation based on the structure, elasticity, and vibrational properties of lizardite (Tsuchiya, 2013). In order to study pressure-dependent chlorine isotopic fractionation in lizardite, we used the P31m space group and atomic positions from the Lizardite 1T polytype {$Mg_3Si_2O_5(OH)_4$} (Mellini and Viti, 1994). In this paper, four different models for lizardite have been considered to better assess the influence of chlorine substitution of inner and inter-layer OH sites on the calculated reduced partition function ratios for $^{37}Cl/^{35}Cl$ in lizardite, as described below: (i) Lizardite-A0 is a unit cell where all the hydroxyl groups were replaced by Cl atoms, with the chemical formula of $Mg_3Si_2O_5Cl_4$; (ii) Lizardite A1, A2 and A3 were built from supercells, replacing one inner OH by one Cl atom for A1, one inter-layer OH by one Cl atom for A2, and one inner OH and one inter-layer OH by two Cl atoms for A3. The number of total atoms in individual A1, A2 and A3 supercells is 143, 143, 142, respectively. The pressure dependence of chlorine isotopic fractionation in lizardite was investigated for 0, 0.05, 0.5, 2.5 and 5.0 GPa.

2.4. Error estimation

The calculation accuracy of β-factor values depends primarily on two factors, the uncertainty associated with the calculated phonon frequencies between isotopomers using density functional perturbation theory (DFPT) and the uncertainty related to anharmonic effects (Méheut et al., 2007). The uncertainty in the calculation of phonon frequencies by DFT, at the PBE level, leads to a systematic relative error of about 5%, which is similar to that affecting the calculation of β-factors. The uncertainty arising from anharmonic effects in minerals is relatively small, whereas there is strong anharmonic effect for water leading to a relative error of -5% (Méheut et al., 2007). The relative error associated with the calculation of the phonon frequency in this study is estimated to be ±4% (Figure S1), which is similar to that obtained by Méheut et al. (2007). Consequently, the relative error for the β factor and that for the fractionation factor ($\Delta_{A\text{-}B} = 1000\ln\alpha_{A\text{-}B}$) of the minerals are estimated to be ±4% and ±8%, respectively. The overall absolute errors for $\Delta_{\text{lizardite-halite}}$ are ±0.41‰, ±0.11‰, ±0.04‰ at 300 K, 600 K and 1000 K, respectively.

3. Results

3.1. Equilibrium chlorine isotope fractionation at ambient conditions

To assess the accuracy of the theoretical estimates, the calculated lattice parameters and vibrational frequencies of the minerals mentioned above were compared to their experimentally determined values (Table S1, Figure 3). The good agreement between the two sets of data shows that the PBE functional and norm-conserving pseudopotentials can be used to reliably predict the isotopic fractionation of chlorine between pairs of these minerals.

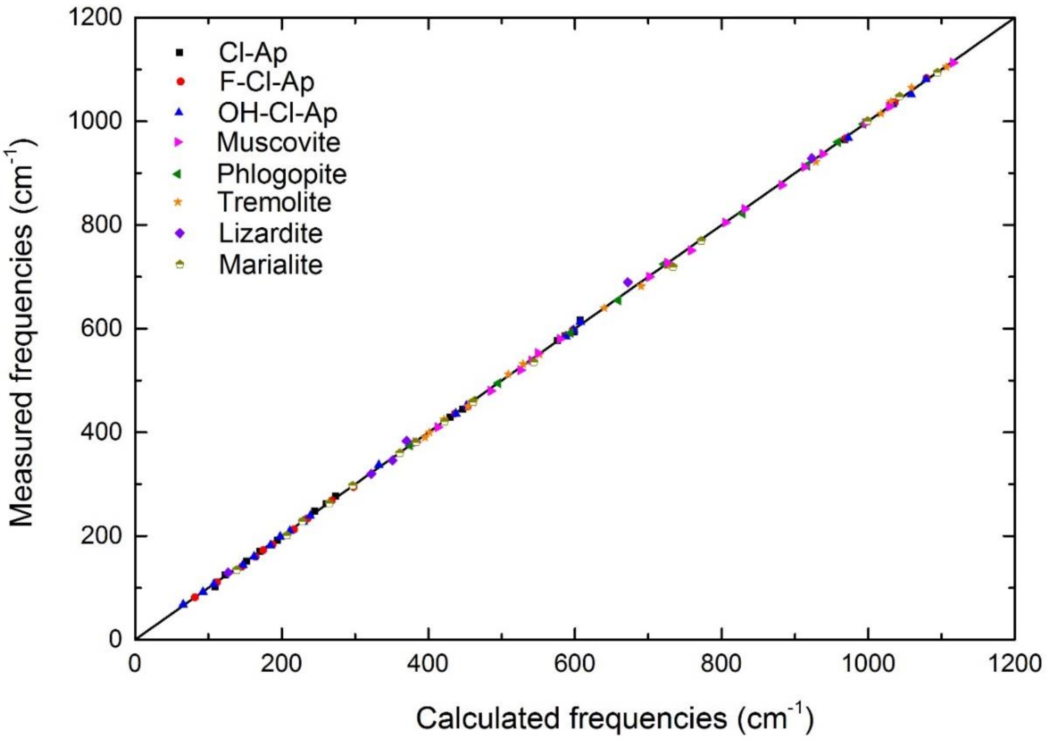

Figure 3. Comparison of calculated and experimentally determined vibrational frequencies for chlorine-bearing minerals. The measured vibrational frequencies are from previous studies, as listed in Table S2 in the Appendix.

The calculated reduced partition function ratios (1000lnβ) for chlorine-bearing minerals at 0 GPa are shown in Figure 4. The values of 1000lnβ for ^{37}Cl/^{35}Cl decrease in the order lizardite > phlogopite > muscovite > tremolite > fluoro-chlorapatite > hydroxyl-chlorapatite > chlorapatite > sodium chloride > marialite. The β values for halite, chlorapatite and lizardite estimated in this study were compared to those calculated by Schauble et al. (2003) and Balan et al. (2019) for the temperature range, 300 K to 1000 K (Figure 4). Balan et al. (2019) built a unit-cell of the periodic model of lizardite with a 2×2×2 supercell containing 112 atoms, and satisfactorily reproduced the chlorine substitution for sites at an inner-OH or an inter-layer OH. The β values of lizardite A0 determined in the current study are close to those for the lizardite Cl2 reported by Balan et al. (2019); at 450 K the difference is 0.07‰ and at 800 K it is 0.01‰. Furthermore, the differences in the β values of lizardite A2 (this study) and lizardite

Cl1 (Balan et al. (2019) are negligible, e.g., 0.004‰ at 450 K (Figure 4). In addition, comparisons for other minerals, such as halite and chlorapatite, show that the difference in the β values are less than 0.5‰ at 300 K and is even smaller, ~0.1‰ at 600 K; the latter might be due to a computational error for β factors of minerals obtained using different exchange-correlation functionals. At ambient P-T conditions, the 1000lnβ factors correlate negatively with the metal-Cl bond length of the minerals (Figure 5a). The same observation was made for the equilibrium fractionation of Ca isotopes (Huang et al., 2019). Minerals containing trivalent metals (e.g., Al^{3+}) with short bonds between these metals and chlorine were shown to have higher β factors than minerals with monovalent metal ions (e.g., Na^{+}) and long bonds between these cations and Cl. The β factors of minerals in which Cl is bonded to Mg (lizardite, phlogopite and tremolite) are similar, as are the β factors for minerals in which Cl is bonded to Ca (apatite group minerals). These observations are in excellent agreement with those for chlorine isotopic fractionation reported by Schauble et al. (2003) and Balan et al. (2019). In order to evaluate the correlation of β factors with the cation-chlorine bond strength of the minerals studied, we calculated the latter using the relationship:.

$$C_{ct-Cl} = \frac{V}{(r_{ct}+r_{Cl})CN_{ct}} \qquad \text{(Eq. 6)}$$

where $C_{ct\text{-}Cl}$ is the cation-chlorine bond strength, CN_{ct} is the coordination number of the cation, r is the ionic radius of the cation and chloride and V is the oxidation state of the cations (Zheng, 1996) . With the exception of muscovite, the 10^3lnβ values correlate positively with the metal-Cl bond strength of these minerals (Figure 5b). The reason for the anomalous behavior of muscovite is unclear but might be due to the polarization effect of Al^{3+} ions.

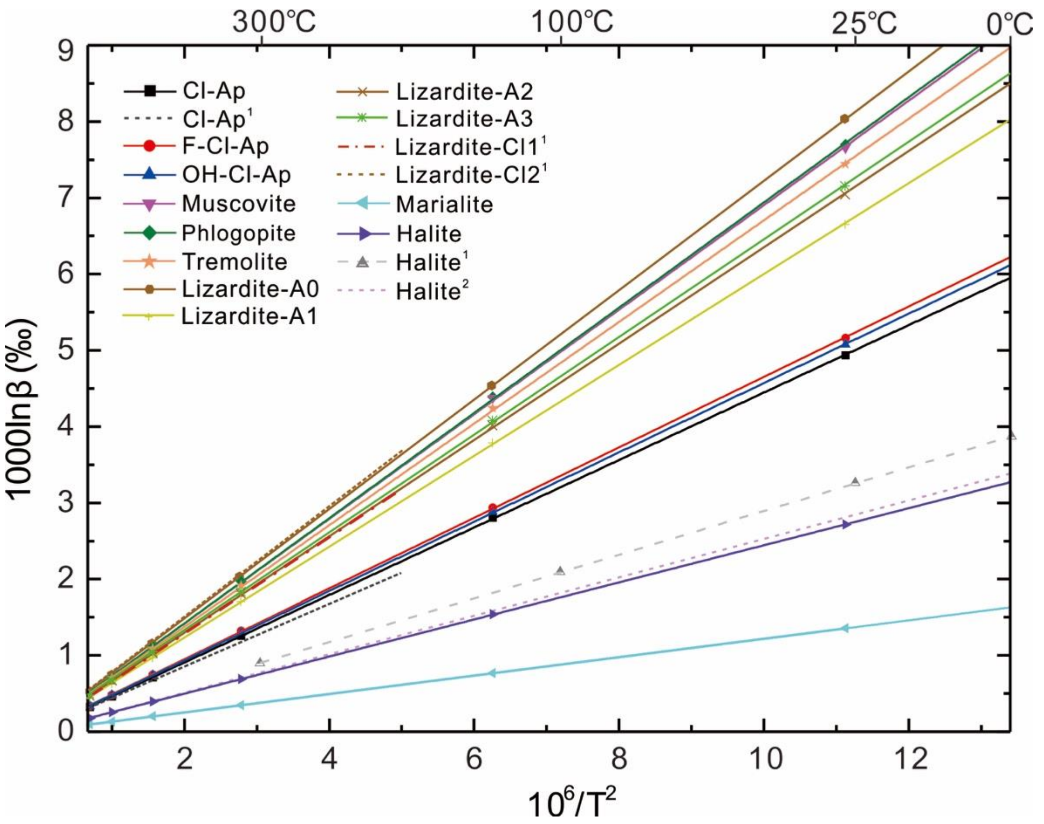

Figure 4. Temperature dependence of the equilibrium reduced partition function ratios $10^3\ln\beta$ for chlorine isotopes in chlorine-bearing minerals at 0 GPa. The data for halite[1] are from Schauble et al. (2003). The data for Cl-Ap[1], halite[2] and lizardite-Cl1/Cl2[1] are from Balan et al. (2019).

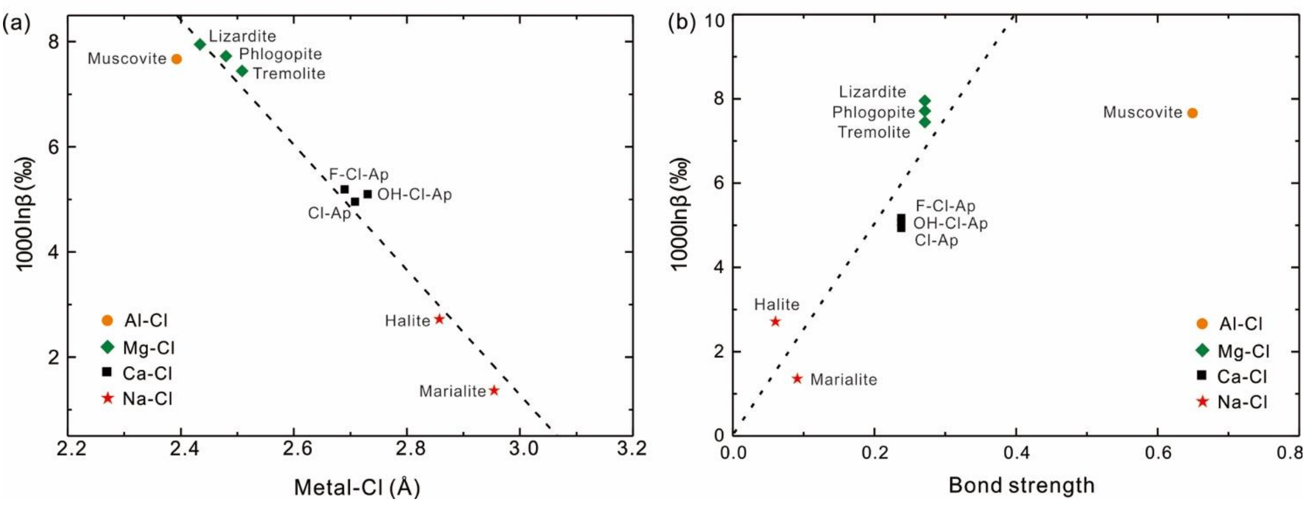

Figure 5. Equilibrium reduced partition function ratios $10^3\ln\beta$ as a function of the metal-Cl bond length (a) and the metal-Cl bond strength based on Eq. 6 (b) in chlorine-bearing minerals at ambient P-T conditions.

Based on the results of a first-principles calculation, the Ca and Mg concentrations in orthopyroxene and carbonate minerals are highly sensitive to the lengths of the metal-O bond (Feng et al., 2014; Wang et al., 2017). To better understand the solid-solution properties and ordering scheme affecting chlorine isotope fractionation in OH-F-Cl apatite, we examined the effect of Cl concentration on the Ca-Cl bond length and equilibrium fractionation of chlorine isotopes among apatite group minerals ($Ca_5(PO_4)_3((F,Cl)_xOH_{1-x})$). As shown in Figure 6, the 1000lnβ factors decrease linearly with increasing *x* (i.e., Cl content) from 1/4 to 3/4, and then increase slightly as *x* approaches unity. A reverse trend for the average Ca-Cl bond length versus. *x* is also observed, confirming that the strength of the Ca-Cl bond exerts an important control on the equilibrium fractionation of chlorine isotopes in apatite group minerals. Considering the relatively large difference of 0.61‰ in 1000lnβ at 300 K, the chemical composition of apatite group minerals should be taken carefully into account in interpreting low-temperature geochemical processes.

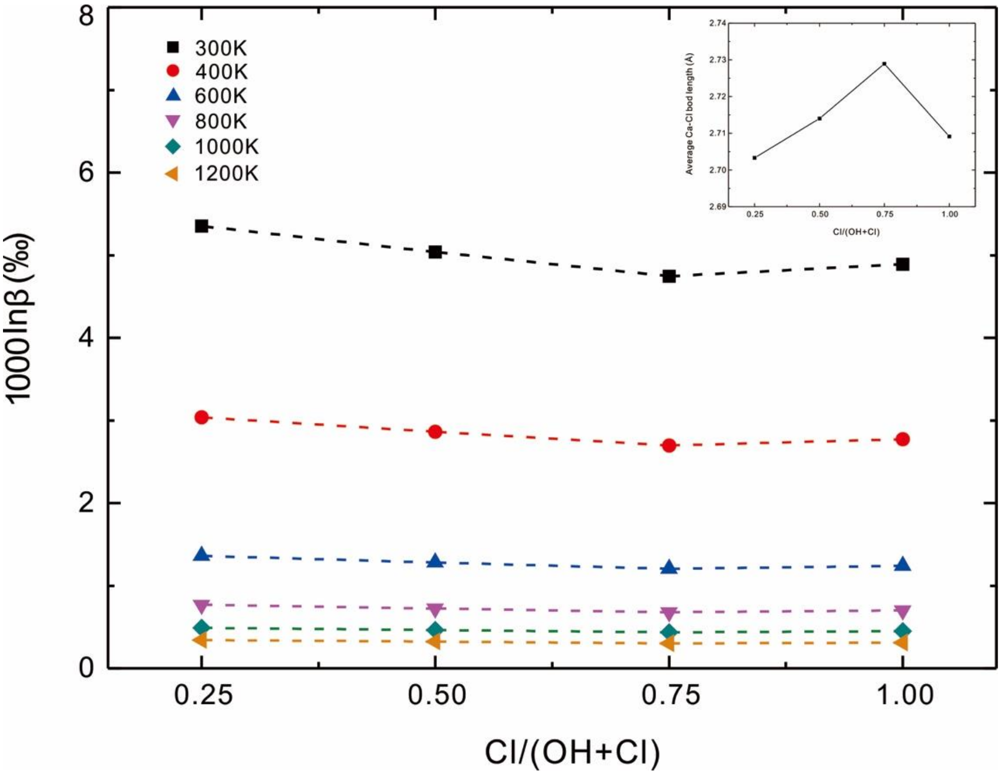

Figure 6. The dependence of $10^3\ln\beta$ of apatite group minerals on Cl/(OH+Cl) at various temperatures. The insert shows the average Ca-Cl bond length versus Cl/(OH+Cl) at ambient P-T conditions.

3.2. Pressure effects on chlorine isotope fractionation in minerals

The effect of pressure on chlorine isotope fractionation is of interest because all of the minerals investigated in this study are stable over wide ranges of pressure. As shown in Figure S2, the unit cell volume of each mineral decreases and the density increases with increasing pressure. The calculated slope of unit cell volume versus pressure for apatite and lizardite is approximately the same as that obtained experimentally by Comodi (2001), Mellini and Zanazzi (1989) and Hilairet et al. (2006), indicating the robust nature of our theoretical calculations.

The average Ca-Cl, Na-Cl, Mg-Cl and Al-Cl bond lengths in several chlorine-bearing minerals are shown as a function of pressure in Figure 7. In general, the metal-chlorine bond length decreases with increasing pressure, but the slopes are not all uniform. The slope for the Na-Cl bond length in marialite becomes increasingly negative above 2.5 GPa, whereas the slope for the Ca-Cl bond length of hydroxyl-chlorapatite remains almost constant at pressures greater than 5 GPa. Slopes for the metal-Cl bond lengths of muscovite, phlogopite and tremolite decrease slightly with increasing pressure.

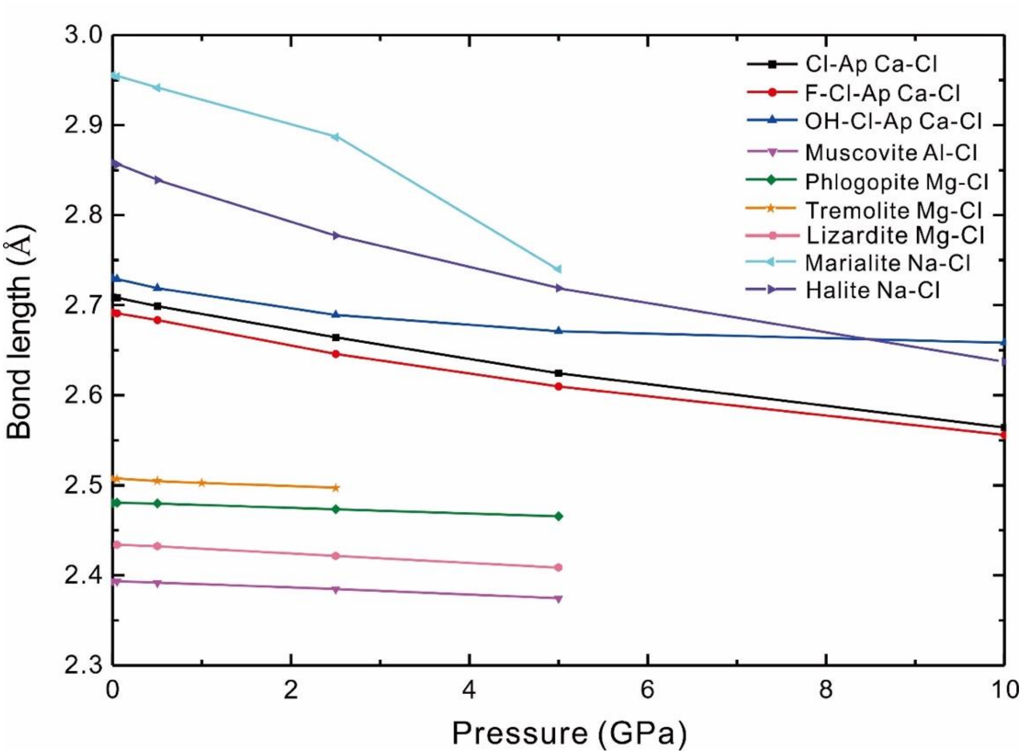

Figure 7. Variations in the average metal-Cl bond length for chlorine-bearing minerals with increasing pressure at static conditions.

4. Discussion

4.1. P-T dependence of chlorine isotope fractionation among chlorine-bearing minerals

At 300 K, the differences in 1000lnβ values for chlorine isotopes at 10 GPa relative to those at ambient pressure are 3.13‰ (fluoro-chlorapatite), 3.06‰ (chlorapatite) and 2.02‰ (hydroxyl-chlorapatite) (Figure 8, Table S3), showing that fluoro-chlorapatite is the most pressure-sensitive member of the apatite group. Halite is the most pressure-sensitive of all the minerals considered with a difference in its 1000lnβ value at 10 GPa relative to ambient pressure of 3.30‰. At 800 K and 2.5 GPa, the calculated reduced partition function ratios (lnβ) follow the sequence, lizardite > muscovite > phlogopite > tremolite > fluoro-chlorapatite > chlorapatite > hydroxyl-chlorapatite > halite > marialite, whereas the sensitivity to pressure ($10^3\ln[\beta_P/\beta_0]$) follows the sequence, halite > fluoro-chlorapatite > chlorapatite > marialite > hydroxyl-chlorapatite > lizardite > tremolite > muscovite > phlogopite.

An expression for the β-factors of the above minerals, based on their thermodynamic properties, was derived using the first-order thermodynamic perturbation theory of Polyakov and Kharlashina (1994) expressed in Eq. 7:

$$\left(\frac{\partial\beta}{\partial P}\right)_T = \frac{\gamma_{th}}{B_T}\left[(\beta-1)+\frac{\Delta m}{m^*}\frac{C_V-3R}{2R}\right] \qquad \text{(Eq. 7)}$$

where γ_{th} is the thermal Grüneisen parameter, which depends only slightly on temperature and is essentially independent of pressure, B_T is the isothermal bulk modulus expressed as $B_T = -\left(\frac{\partial lnV}{\partial P}\right)_T^{-1}$, C_V is the molar heat capacity of a crystal, m and m^* are the masses of the light and heavy isotope atoms and $\Delta m = m^* - m$ and R is the gas constant.

The effect of pressure on the equilibrium isotope fractionation factors is due to i) a difference in the thermal Grüneisen parameter (γ_{th}) of the minerals, ii) differences in the values of the derivatives $\frac{\partial\beta}{\partial P}$; and iii) differences in the isothermal bulk moduli (Polyakov and Kharlashina, 1994). Given that γ_{th} and C_V are constants for a particular mineral, and that B_T is a linear function of P (i.e., $B_T = a + bP$) (Polyakov and Kharlashina, 1994), integration of Eq. 7 gives the following expression:

$$ln\frac{\left(\beta-1+\frac{\Delta m}{m^*}\frac{C_V-3R}{2R}\right)}{\left(\beta_0-1+\frac{\Delta m}{m^*}\frac{C_V-3R}{2R}\right)} = \frac{\gamma_{th}}{b}\ln\left(1+\frac{b}{a}P\right) \qquad \text{(Eq. 8)}$$

As a is generally >> b (Polyakov and Kharlashina, 1994) and the term of $\frac{\Delta m}{m^*}\frac{C_V-3R}{2R}$ is << 1, Eq. 8 can be simplified as:

$$ln\frac{(\beta-1)}{(\beta_0-1)} = A + \gamma_{th}\frac{1}{a}P \qquad \text{(Eq. 9)}$$

This equation predicts a linear dependence of the β-factors on pressure, as has been shown in this study for $^{37}Cl/^{35}Cl$ in chlorine-bearing minerals (Figure 8), and also for the β-factors for D/H in brucite (Horita et al., 2002). Quantitative expressions for 1000lnβ as functions of pressure at low temperature (300 K) and high temperature (1000 K) are listed in Table S3. The theoretical predictions indicate that pressure-induced shifts cannot be ignored in interpreting stable chlorine isotopic ratios. Similar pressure effects have been reported for Mg isotope fractionation among garnet, clinopyroxene, orthopyroxene, and olivine, for O isotope fractionation between rutile and calcite, for C isotope fractionation among graphite, calcite and diamond, and H isotope fractionation in the brucite-water system (Huang et al., 2013; Polyakov and Kharlashina, 1994; Horita et al., 2002).

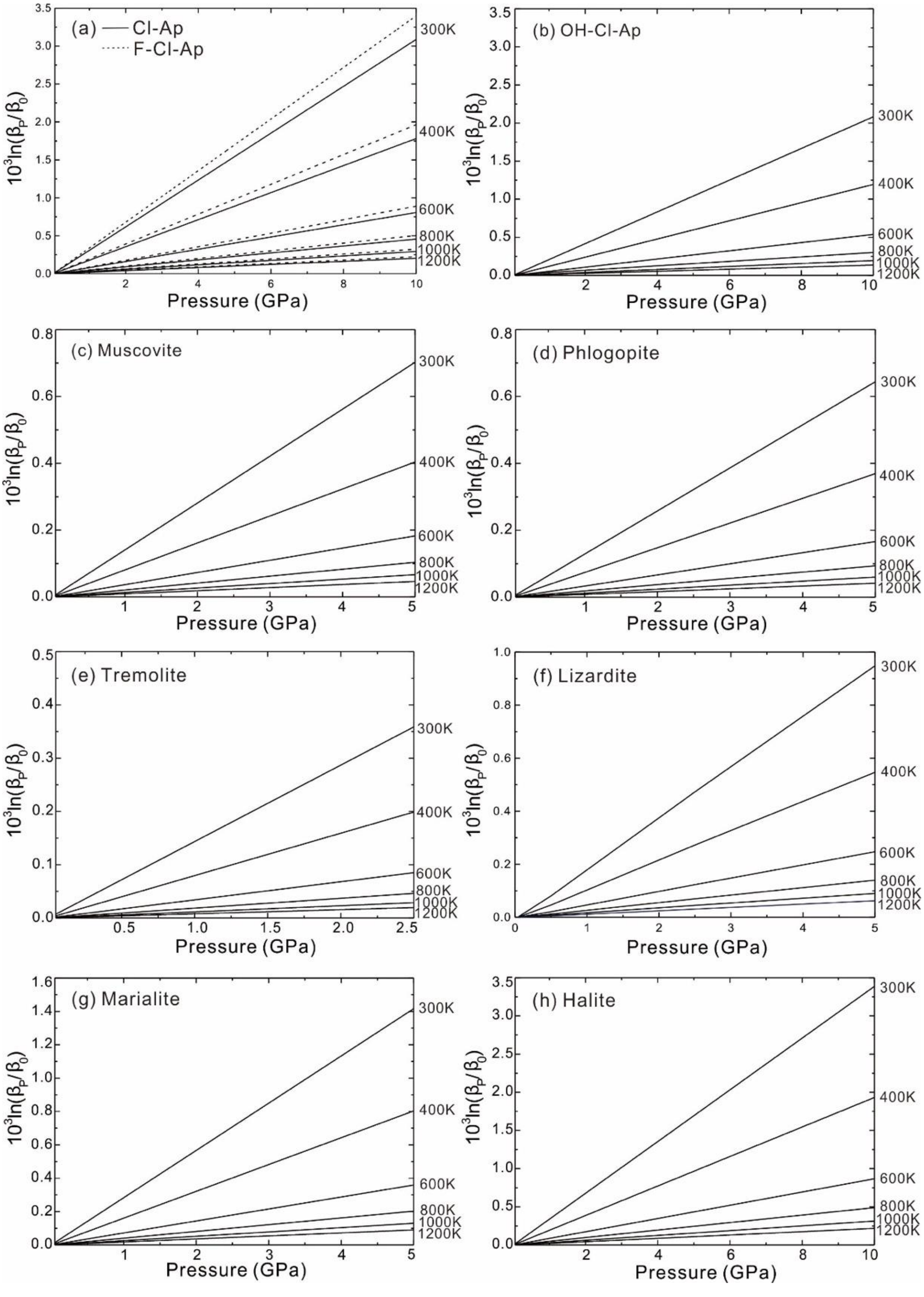

Figure 8. The dependence of the reduced partition function ratios, $10^3\ln(\beta_P/\beta_0)$, on pressure for the $^{37}Cl/^{35}Cl$ ratio of chlorine-bearing minerals (apatite, muscovite, phlogopite, tremolite, lizardite, marialite, halite) as a function of pressure. The term β_0 represents the calculated reduced partition function at 0 GPa.

Figure 9a illustrates the calculated Cl isotope fractionation ($\Delta^{37}Cl_{A-B} = 1000\ln\beta_A - 1000\ln\beta_B$) between Cl-bearing minerals (A) and halite (B) as a function of reciprocal temperature for 0 and 2.5 GPa, and provides insights into the equilibrium chlorine isotope fractionation among cogenetic Cl-bearing minerals. Except for marialite, the values of $\Delta^{37}Cl_{A-B}$ are positive at 0 and 2.5 GPa. At conditions of sedimentary rock formation (300 K, 1×10^{-4} GPa), the value of $\Delta^{37}Cl_{fluoro-chlorapatite-NaCl}$ is about +2.5‰. In contrast, a $\Delta^{37}Cl_{fluoro-chlorapatite-NaCl}$ value of ~ +0.20‰ is estimated for the conditions at which fluoro-chlorapatite was intergrown with NaCl in carbonatite-hosted melt inclusions (1200 K, 2.5 GPa) (Kamenetsky et al., 2015).

4.2. P-T dependence of chlorine isotope fractionation between chlorine-bearing mineral and aqueous chloride

Previous studies have demonstrated that the pressure dependence of Li and B isotope fractionation in aqueous fluids matches well the shifts of pressure-induced vibrational frequencies (Kowalski and Jahn, 2011; Kowalski et al., 2013). Using the measured vibrational frequency shifts of the $Cl^{-}\cdots O\text{-}H$ stretching band in NaCl solution with pressure (Wang et al., 2013), we derived the relative shifts in the (β-1) factor employing the relationship of $(\beta-1) \propto \upsilon^2 \sim \upsilon_0^2 + 2\upsilon_0 \Delta \upsilon$ (Schauble, 2004). As shown in Figure S3, the calculated (β -1) values for aqueous chloride show a linear dependence on pressure in the range from 0.1 to 3.12 MPa, (β -1) = 1.55-0.013*P* (MPa)‰, and then remain almost constant at higher pressure (> 3 MPa) and ambient temperature. It therefore follows that the pressure effect on chlorine isotope fractionation in aqueous fluids is insignificant and can be neglected at high temperature.

Based on the experimental results of Eggenkamp et al. (1995), Schauble et al. (2003) estimated values of 2.1-3.0‰ for $1000\ln\beta_{brine}$ and a value of +0.26‰ for $\Delta^{37}Cl_{halite-aqueous\ Cl}$ at 295 K, which is lower than the 1000lnβ value of 3.13 for aqueous chloride from the calculations of Czarnacki and Halas (2012). With reference to the median value of 2.55 for 1000lnβ in aqueous chloride at 295 K by Schauble et al. (2003), the over-estimates of $1000\ln\beta_{Cl^-}$ by Czarnacki and Halas (2012) were corrected by following the procedure of Rustad et al. (2010) and Kowalski et al. (2013). Assuming that $1000\ln\beta \propto T^{-2}$ and a value of Δ1000lnβ of -0.58‰ as the difference between the 1000lnβ values of Schauble et al. (2003) and Czarnacki and Halas (2012) at 295 K, the 1000lnβ values reported by Czarnacki and Halas (2012) were overestimated by $\Delta 1000\ln\beta = (-0.58) \times (\frac{295}{T})^2‰$. The value of 1000lnβ of Czarnacki and Halas (2012) so corrected is plotted in Figure S4. The temperature dependence of $10^3\ln\beta_A$-$10^3\ln\beta_B$ for $^{37}Cl/^{35}Cl$ between different chlorine-bearing minerals and aqueous chloride were derived as shown in Figure 9b. This enables the $\delta^{37}Cl$ values of individual minerals equilibrating with aqueous fluid at different P-T conditions to be determined. For example, the data predict that the $\delta^{37}Cl$ value of fluoro-chlorapatite on the seafloor that is in isotopic equilibrium with seawater ($\delta^{37}Cl_{SMOC}$ of 0.0‰) is ~ +2.7‰. In contrast, chlorapatite crystallizing from a hydrothermal fluid containing chloride with a $\delta^{37}Cl$ value of 0‰ would have a $\delta^{37}Cl$ value of +0.63‰ at 600 K and 30 MPa. The $\delta^{37}Cl$ values in mantle minerals are more difficult to predict, as addressed below.

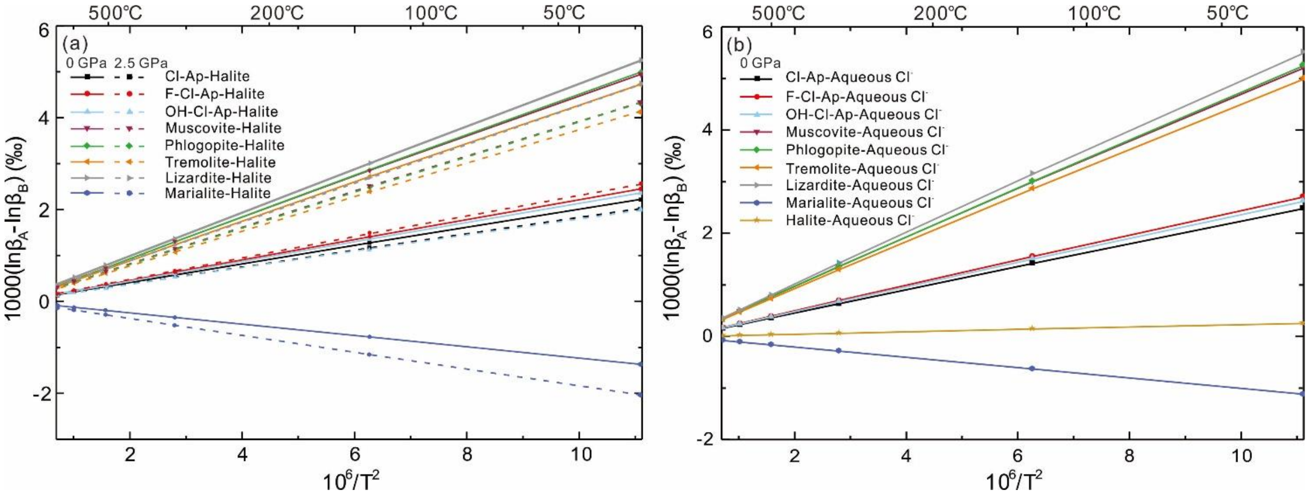

Figure 9. (a) Temperature dependence of $10^3\ln\beta_A$-$10^3\ln\beta_B$ for $^{37}Cl/^{35}Cl$ between different chlorine-bearing minerals (A) and halite (B) at 0 and 2.5 GPa. The solid lines are for 0 GPa and the dotted lines for 2.5 GPa. (b) Temperature dependence of $10^3\ln\beta_A$-$10^3\ln\beta_B$ for $^{37}Cl/^{35}Cl$ between different chlorine-bearing minerals (A) and aqueous chloride (B) at ambient pressure.

4.3. Controls on chlorine isotope heterogeneity in the mantle

4.3.1. Chlorine isotope heterogeneity in metamorphic minerals in subduction-zones

As discussed in the introduction to this paper, the $\delta^{37}Cl$ values of mantle-derived materials are characterized by extreme heterogeneity as deduced from MORB, OIB and mantle xenoliths, for which the values range from -1.9‰ to +3.0‰. However, as mentioned above, whether the subduction of crustal materials into the mantle is partly or wholly responsible for this extreme $\delta^{37}Cl$ heterogeneity is still strongly debated.

From Figure 9a, it is evident that the $\Delta^{37}Cl_{mineral-NaCl}$ values for apatite, tremolite and phyllosilicates (muscovite, phlogopite, lizardite) increase with decreasing temperature at pressures of 0-2.5 GPa; they are positive up to at least 1200 K. Greenschist-facies grade alteration due to hydrothermal circulation of seawater extends to a depth of ~3.5 km in MORB crust, beneath a water column 2.6 to 4 km in depth. With reference to the lithostatic pressure of ca. 0.17 GPa at this depth (Petrini and Podladchikov, 2000), values of $\Delta^{37}Cl_{mineral-NaCl}$ for tremolite, phyllosilicates and apatite range from +0.56 to +1.33‰ at 0.17 GPa and 600 K (a likely temperature for the alteration).

At the conditions of subduction illustrated in Figure S5 (for example, 1300K and > 2.5 GPa), the values of $\Delta^{37}Cl_{mineral-NaCl}$ for tremolite, phyllosilicates and apatite are small, < +0.31‰. As the pressure effect is negligible at high temperature, the value of $\Delta^{37}Cl_{NaCl-aqueous\ Cl}$ in supercritical NaCl-H_2O at 1200 K was estimated to be +0.01‰. Assuming the processes reach equilibrium and the fluids present during HT to UHT metamorphism have $\delta^{37}Cl$ values close to SMOC ($\delta^{37}Cl$ = 0.0‰), secondary Cl-bearing minerals formed under these conditions would have small positive values of δ^{37}Cl (e.g., +0.34‰ for tremolite in a shallow subduction zone and +0.38‰ for phlogopite in a deep subduction zone). The predicted δ^{37}Cl values of fluoro-chlorapatite, muscovite and marialite in various metamorphic facies are shown in Figure 10. The δ^{37}Cl values of fluoro-chlorapatite in the greenschist and garnet-ecologite facies are estimated to be +0.26‰ and +0.74‰, respectively, and those of muscovite in the lawsonite-eclogite and amphibolite facies to be +0.48‰ and +0.67‰, respectively. By contrast, the δ^{37}Cl values of marialite are slightly negative, -0.16‰ and -0.12‰ in the amphibolite and granulite facies, respectively.

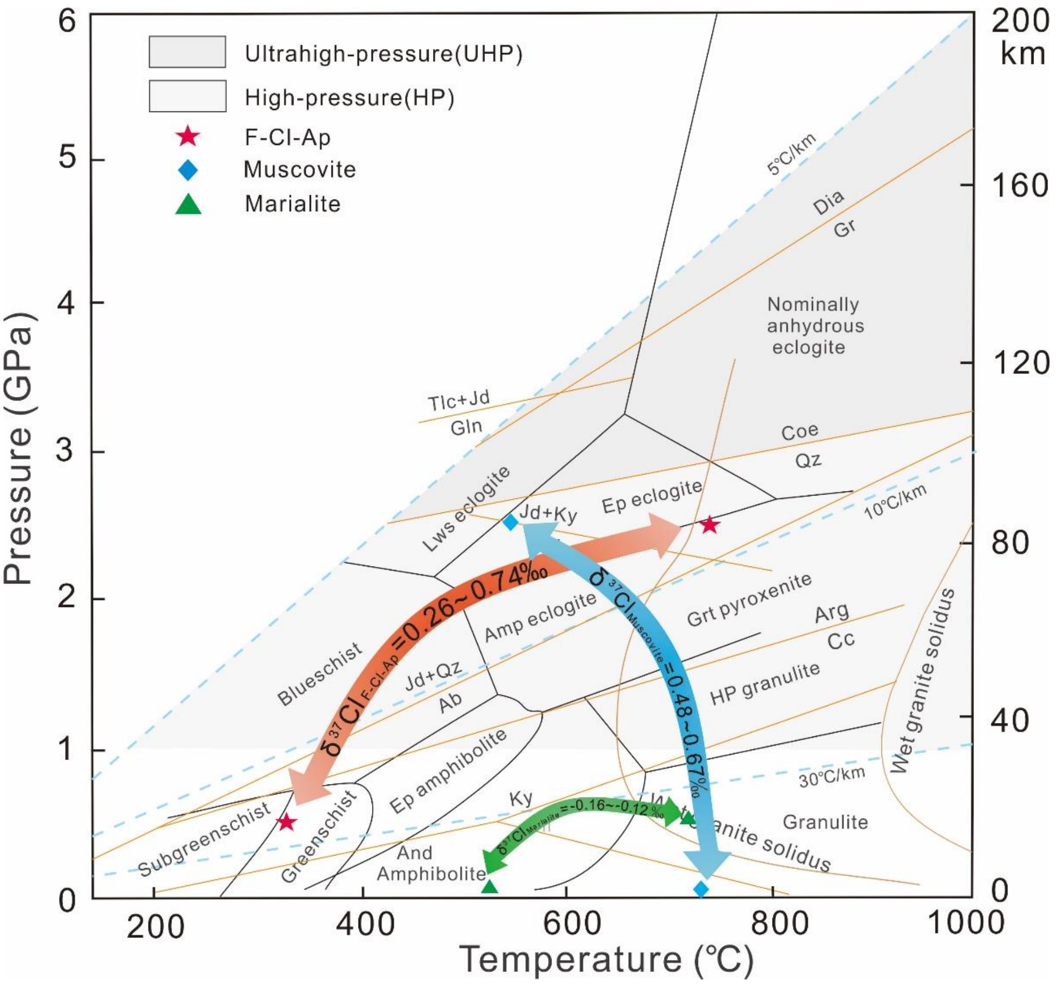

Figure 10. The δ^{37}Cl values of hydrous minerals in different metamorphic facies including those of subduction-zones. The dark-grey area corresponds to UHP metamorphism above the coesite/quartz

transition boundary, whereas the light-grey area denotes HP metamorphism below the coesite/quartz transition line (modified after Zheng and Chen, 2017).

The data presented above indicate that variations in the δ^{37}Cl values of hydrous minerals during metamorphism are relatively minor over a wide range of P-T conditions. For the purpose of the current study, the simplest assumption is that the chloride in the subducting MORB has δ^{37}Cl values close to SMOC, although it should be noted that alteration of MORB as a result of interaction with seawater during seafloor spreading may locally affect its δ^{37}Cl value substantially. During the subduction of crustal rocks, however, aqueous fluids are generated not only by the prograde breakdown of hydrous minerals but also by the exsolution of molecular water and structural hydroxyl from nominally anhydrous minerals (NAMs) (Zheng, 2009; Zheng and Hermann, 2014). As water is highly incompatible during partial melting of crust and mantle rocks (Zheng and Hermann, 2014) and chloride has a strong preference for the fluid over the melt, fluids enriched in chloride with variable δ^{37}Cl signatures participate extensively in metamorphism. It is also important to consider the contribution of sediments in evaluating chlorine incorporation in mantle materials during subduction. This is because the chlorine flux from sediments and pore water is twice that of oceanic crust during subduction (Eggenkamp, 2014). For the reasons given above, chlorine isotopic fractionation may be considerable as a result of the exchange of chloride between metamorphic minerals and fluid in shallow and deep subduction zones (as shown schematically in Figure 11a). Indeed, the δ^{37}Cl values of metamorphic minerals originating from hydrothermally altered MORB may range from +1 to +3‰. We distinguish between a primary mantle with a low Cl content and a secondary mantle fertilized by subduction that has a much higher chlorine content. From the data of Eggenkamp (2014), it is evident that the secondary mantle, with a higher chlorine content, is characterized by higher δ^{37}Cl values. This observation is consistent with the theoretical predictions from this study that the minerals undergoing metamorphism during subduction are enriched in ^{37}Cl relative to the metamorphic fluid. In contrast, subduction of sediments with the original δ^{37}Cl signatures of -8‰ to 0‰ to deep subduction zones may might produce δ^{37}Cl from -7‰ to +1‰.

4.3.2. Estimation of δ^{37}Cl for the bulk mantle

A δ^{37}Cl value for the bulk mantle can be estimated via mass balance, from the concept of the chlorine cycle and the annual Cl isotopic fluxes from continental crust, oceanic crust, ocean, sediments and mantle (Figure 11b) using the following equation:

$$\{(\delta^{37}Cl_{OC} \times F_{OC-Mantle} + \delta^{37}Cl_{SP} \times F_{SP-Mantle}) - \delta^{37}Cl_{Mantle}(F_{Mantle-CC} + F_{Mantle-Ocean} + F_{Mantle-OC})\} \times t = \delta^{37}Cl_{Mantle} \times m_{Cl\ in\ Mantle} \quad \text{(Eq. 10)}$$

where $F_{A\text{-}B}$ is the annual flux of Cl from Reservoir A to Reservoir B, 10^9 kg·year^{-1}; $m_{\text{Cl in mantle}}$ is the total mass of Cl in mantle reservoir, 6.59×10^{19} kg (McDonough, 2000); *t* is the period of the chlorine cycle from the mantle to the surface reservoir. The abbreviations of OC, CC and SP represent ocean crust, continental crust and sediment and pore water.

Hay et al. (2006) prepared a detailed inventory of all evaporites deposited since the Ediacaran and concluded that there have been significant changes in the mean salinity of the ocean and that it declined progressively during the Phanerozoic. In applying equation 10, we have defined *t* as the beginning of the Ediacaran at ca. 635 Ma, a time when a large amount of chlorine began to flow from the mantle to the surface reservoir. Based on the δ^{37}Cl values reported for sediment and pore water (−8‰ to 0‰), and oceanic crust (-2‰ to 0‰) (Barnes and Sharp, 2017), and the annual fluxes of chlorine among those reservoirs (Eggenkamp, 2014), the δ^{37}Cl value for the bulk mantle is estimated to be in the range -0.69‰ to -0.37‰; the mean value is -0.53±0.16‰ from an iterative calculation repeated more than

10000 times (Figure 11b, 12). Our calculations therefore show that the bulk mantle is slightly depleted in ^{37}Cl with a δ^{37}Cl value of ca. -0.53±0.16‰ relative to SMOC. This agrees well with δ^{37}Cl values measured from terrestrial mantle-derived material and the most pristine type C chondrites, which form a peak between -0.3‰ to -0.1‰ (Sharp et al., 2013; Eggenkamp and Koster van Groos, 1997). Finally, we conclude that the heterogeneous distribution of δ^{37}Cl values represented by this range resulted from metamorphism related to subduction over a range of P-T conditions.

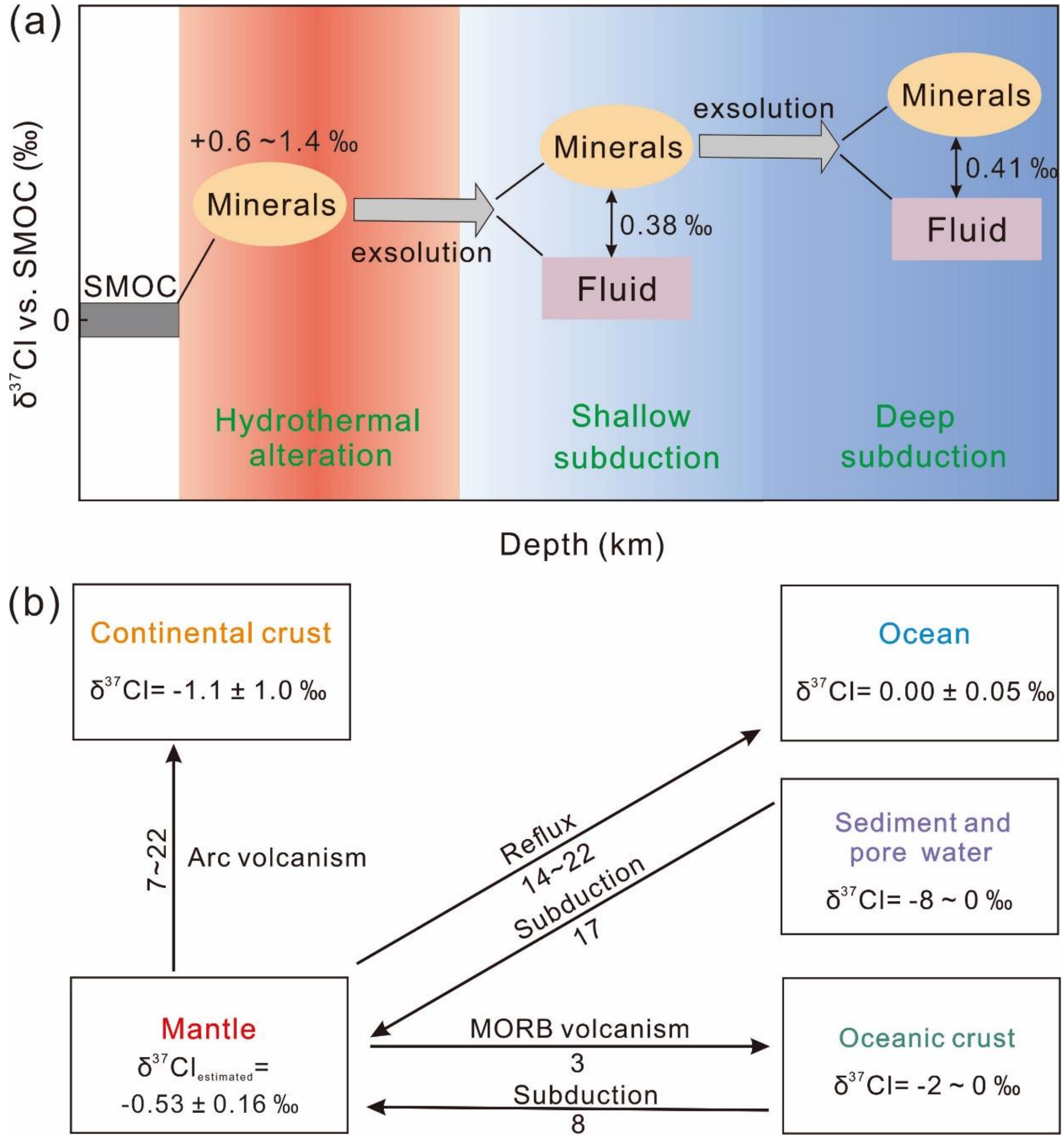

Figure 11. (a) Variation of δ^{37}Cl as a result of processes related to hydrothermal alteration near spreading centers and subduction zones; (b) δ^{37}Cl values of bulk mantle derived from the exchange of chlorine among continental crust, oceanic crust, ocean, sediment. The chlorine fluxes (simplified, 10^{12} g·year^{-1}) are from Eggenkamp (2014) and the δ^{37}Cl values of the individual reservoirs are from Barnes and Sharp (2017).

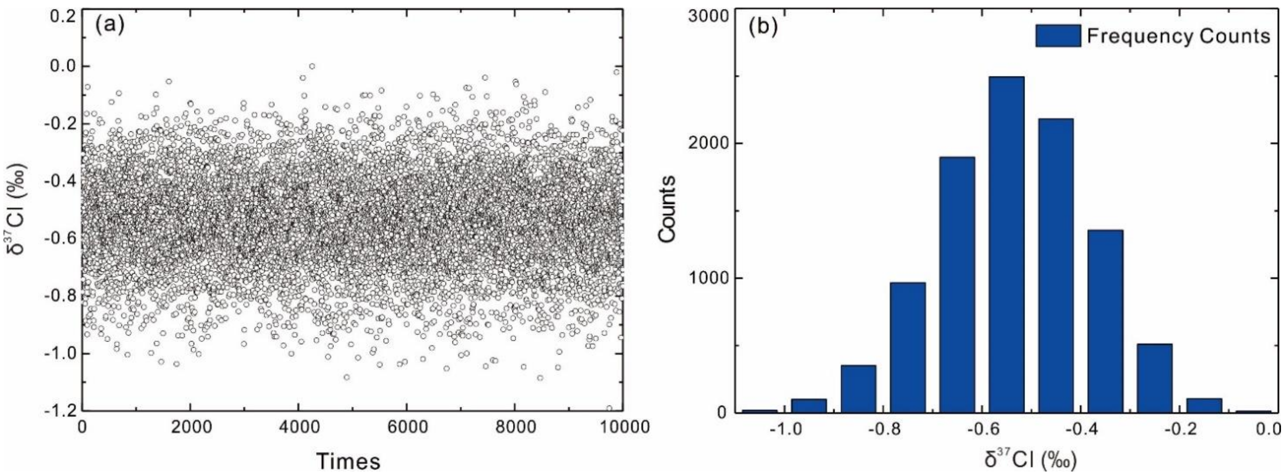

Figure 12. (a) Estimated δ^{37}Cl values of the bulk mantle from an iterative calculation based on mass balance; (b) Frequency distribution δ^{37}Cl values in the bulk mantle.

5. Conclusions

An evaluation of equilibrium chlorine isotope fractionation among chlorine-bearing minerals (apatite-group minerals, muscovite, phlogopite, tremolite, lizardite, marialite, sodium chloride) using first-principles calculations leads to the following conclusions:

(1) At ambient P-T conditions, the ^{37}Cl enrichment in minerals follows the order, lizardite-A0 > phlogopite > muscovite > tremolite > lizardite-A3 > lizardite-A2 > lizardite-A1 > fluoro-chlorapatite > hydroxyl-chlorapatite > chlorapatite > sodium chloride > marialite. The 1000lnβ factors are strongly correlated with the metal-Cl bond length and the bond strength of the minerals, such that, in minerals in which chlorine is bonded to trivalent metals (e.g., Al^{3+}), the metal-Cl bonds are shorter and the β factors higher than for minerals, in which the chlorine is bonded to monovalent metals (e.g., Na^{+}) and metal-Cl bonds are long.

(2) Pressure affects the chlorine isotope fractionation for the minerals studied due to the integrated effects of the adjacent atomic environment and the crystal sites of the chlorine atoms, compressibility and the Cl-metal coordination numbers. As a result, the sensitivity to pressure, expressed as $10^3\ln\beta$, follows the order halite > fluoro-chlorapatite > chlorapatite > marialite > hydroxyl-chlorapatite > lizardite > tremolite > muscovite > phlogopite.

(3) During the subduction of crustal rocks and sediments, slab fluids released by compaction of sediments or dehydration of altered ocean crust are enriched in chloride and other fluid mobile elements. Assuming that equilibrium is reached, the maximum δ^{37}Cl variation in mantle minerals is estimated to be from -6‰ to +3‰, which compares favorably with the measured range of -1.9‰ to +3‰. By comparison, the estimated δ^{37}Cl value for the bulk mantle relative to SMOC is -0.53‰. Based on our modeling of the contributions of chlorine from multiple reservoirs in the broader context of the global chlorine cycle, we propose that the observed heterogeneous distribution of δ^{37}Cl values in mantle materials is the result of isotope fractionation associated with the interaction of aqueous fluids with minerals during metamorphism related to subduction over a range of P-T conditions.

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CAPTIONS OF FIGURES AND TABLE

Figure 1. Chlorine isotope variability in mantle-derived materials (Bonifacie et al. 2007, 2008; Sharp et al., 2007; John et al., 2010). EPR: East Pacific Rise; PAR: Pacific Antarctic Ridge; CRR: Costa Rica Rift; SH: St. Helena; M.: McDonald; E.: Easter; F.: Foundation; P.: Pitcairn; S.: Societies; R.: Réunion.

Figure 2. A series of periodic boundary cell (PBC) models for minerals, presented as top and side views.

Figure 3. Comparison of calculated and experimentally determined vibrational frequencies for chlorine-bearing minerals. The measured vibrational frequencies are from previous studies, as listed in Table S3 in the Appendix.

Figure 4. Temperature dependence of the equilibrium reduced partition function ratios $10^3\ln\beta$ for chlorine isotopes in chlorine-bearing minerals at 0 GPa. The data for halite^1 are from Schauble et al. (2003). The data for Cl-Ap^1, halite^2 and lizardite^1 are from Balan et al. (2019).

Figure 5. Equilibrium reduced partition function ratios $10^3\ln\beta$ as a function of the metal-Cl bond length (a) and the metal-Cl bond strength (b) in chlorine-bearing minerals at ambient P-T conditions

Figure 6. The dependence of $10^3\ln\beta$ of apatite group minerals on Cl/(OH+Cl) at various temperatures. The insert shows the average Ca-Cl bond length versus Cl/(OH+Cl) at ambient P-T conditions.

Figure 7. Variations in the average metal-Cl bond length for chlorine-bearing minerals with increasing pressure at static condition.

Figure 8. The dependence of the reduced partition function ratios, $10^3\ln(\beta_P/\beta_0)$, on pressure for the $^{37}Cl/^{35}Cl$ ratio of chlorine-bearing minerals (apatite, muscovite, phlogopite, tremolite, lizardite, marialite, halite) as a function of pressure. The term β_0 represents the calculated reduced partition function at 0 GPa.

Figure 9. (a) Temperature dependence of $10^3\ln\beta_A-10^3\ln\beta_B$ for $^{37}Cl/^{35}Cl$ between different chlorine-bearing minerals (A) and halite (B) at 0 and 2.5 GPa. The solid lines are for 0 GPa and the dotted lines for 2.5 GPa. (b) Temperature dependence of $10^3\ln\beta_A-10^3\ln\beta_B$ for $^{37}Cl/^{35}Cl$ between different chlorine-bearing minerals (A) and aqueous chloride (B) at ambient pressure.

Figure 10. The $\delta^{37}Cl$ values of hydrous minerals in different metamorphic facies including those of subduction-zones. The dark-grey area corresponds to UHP metamorphism above the coesite/quartz transition boundary, whereas the light-grey area denotes HP metamorphism below the coesite/quartz transition line (modified after Zheng and Chen, 2017).

Figure 11. (a) Variation of $\delta^{37}Cl$ as a result of processes related to hydrothermal alteration near spreading centers and subduction zones; (b) $\delta^{37}Cl$ values of bulk mantle derived from the exchange of chlorine among continental crust, oceanic crust, ocean, sediment. The chlorine fluxes (simplified, 10^{12}

g·year^{-1}) are from Eggenkamp (2014) and the δ^{37}Cl values of the individual reservoirs are from Barnes and Sharp (2017).

Figure 12. (a) Estimated δ^{37}Cl values of the bulk mantle from an iterative calculation based on mass balance; (b) Frequency distribution δ^{37}Cl values in the bulk mantle.

Table 1. Calculation sets for chlorine-bearing minerals.