GEOCHEMISTRY OF AMPHIBOLE FROM ARCHEAN AND EARLY PROTEROZOIC ULTRAMAFIC ROCKS: IMPLICATIONS FOR THE SECULAR EVOLUTION OF THE EARTH'S MANTLE

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INTRODUCTION

Since its formation at 4.5 Ga, the Earth underwent a complex evolution that progressively differentiated its original composition into the reservoirs that we presently know: core, mantle, crust, atmosphere, and hydrosphere. Our knowledge on the composition and differentiation mechanisms active in the Early and Ancient Earth are still fragmentary for the paucity of suitable preserved records. During the Hadean eon, the entire planet was thought to be covered by a magma ocean (*e.g.*, Elkins-Tanton, 2008). After the moon-forming impact, the Hadean experienced ongoing meteoritic bombardment, culminating with the late heavy bombardment in the Eoarchaean (Bottke *et al.*, 2012) that may have facilitated early tectonics (Hansen, 2007). During the freezing of the magma ocean Earth lost much of its early atmosphere (*e.g.*, Pepin & Porcelli, 2006) and, at some point, a steam-rich atmosphere rained liquid water, forever changing the geochemistry of the surface and somehow giving birth to primordial life either during, or shortly after, the Eoarchaean (*e.g.*, Buick *et al.*, 1981). From Archean to the present, systematic changes in crustal composition and magma chemistry have been observed by means of geochemical and petrological studies. Differences between Archean and post-Archean crusts have led to much discussion about the style and rate of Archean tectonics, for which the preponderance of granite–greenstone terranes, the high-Na Trondhjemite–Tonalite–Granodiorite (TTG) plutons, and the peculiar nature of the ultramafic komatiite lavas have to be taken into account (*e.g.*, Condie & Kröner, 2008; Greber *et al.*, 2017). In spite of the paucity of Archean rocks, it is proven that the early differentiation events must have left an indelible mark on the mantle.

The poor knowledge on the Archean mantle composition arises a series of problems spanning from the effective chondritic composition of the Earth (Campbell & O'Neill, 2012) to how volatile elements (hydrogen, oxygen, chlorine, and fluorine) were added to the Earth and how their deep cycle evolved giving origin to life and to the present atmosphere. The imbalance in lithophile elements between the chemical composition of the silicate Earth and that of chondrites has arisen, for example, several geochemical "paradoxes" that led to question about the chondritic Earth composition (Campbell & O'Neill, 2012) or were used to model planetary accretion and better understand how Earth formed and evolved through time. In this context, in order to account for the Nb-Ta imbalance between the composition of the silicate Earth and the chondrites, the involvements of reduced asteroidal building blocks with subchondritic Nb/Ta ratios in the Earth's accretion process has been recently supposed (Münker *et al.*, 2017). However, this and other models are based on the assumption that the Earth's mantle is homogeneously subchondritic in the Nb-Ta composition, assumption that is supported by an extremely limited and questionable dataset (Münker *et al.*, 2003). Another key aspect of mantle evolution since Archean is the secular variability of oxygen fugacity, which is a crucial thermodynamic parameter that controls fundamental processes as planetary differentiation, mantle melting, and possible core-mantle exchange. Although most studies, that largely concentrated on the rocks derived from the upper mantle, have concluded that the mantle $f\text{O}_2$ has remained constant within approximately 1.0 log unit since at least the early Archean (Canil, 1997; Canil & Fedortchouk, 2001; Li & Lee, 2004), some researchers have argued for an increase in modern upper mantle $f\text{O}_2$ since the early Archean by as much as 1.5 log units (*e.g.*, Aulbach & Stagno, 2016). Constraining the evolution of the redox state of the mantle is thus of paramount importance for understanding the chemical evolution of major terrestrial reservoirs, including core and atmosphere.

Even more uncertain are the Archean mantle volatile composition and its secular variation. The mantle composition in atmophile elements (carbon, water) and its evolution are, indeed, of particular importance. Volatile elements have large impact on mantle dynamics and are the building blocks of the molecules at the base of life. Atmophiles are key elements in the structure of amino acids, proteins, nucleic acids, and other molecules vital to life. The general atmophile behaviour of these elements, namely their high volatility and general low solubility in mantle minerals, caused them to be primarily partitioned into the atmosphere during Earth differentiation leaving extremely low concentrations in the Earth's mantle. However, at present, mantle is the only proxy we have to decipher the proto atmosphere and how the conditions became favourable for life. Sometime in the mid- to late Archean (*e.g.*, Farquhar et al., 2011), microbial life developed the ability to perform oxygenic photosynthesis, which uses energy from the sun and raw materials extracted from the geosphere (CO_2 + H_2O) to generate energy and eventually releases oxygen in a gas phase (O_2) as a waste product. Over time these biological processes cumulatively oxygenated the Earth's surface.

The Archean mantle is poorly represented on the present-day Earth. Fragments of the Archean crust (greenstone belts) and mantle are found enclosed in Precambrian cratons and Proterozoic basements. An example of Archean mantle is represented by mantle-derived peridotite bodies enclosed in the gneisses of the Western Gneiss Region, Norway (Brueckner *et al.*, 2002). However, the metamorphic reworking of these rocks almost erased the primary geochemical signature of most elements. Valuable information on the Archean mantle have thus to be extracted from mantle-derived igneous rocks generated by partial melting of Archean mantle sources. In the Archean greenstone belts, different products of mantle melting are found as lavas and sills spanning in composition from tholeiites through Fe-picrites to komatiites.

AMPHIBOLE IN THE ARCHEAN AND EARLY PROTEROZOIC ROCKS

The oldest samples found with igneous amphibole are Late Archean komatiites (*c.a.* 2.7 Ga) from the Agnew-Wiluna belt in Western Australia and from the Abitibi greenstone belt in Canada (Stone *et al.*, 2003; Fiorentini *et al.*, 2012). Other Proterozoic amphibole-bearing ultramafic samples considered in this work derive from different units of the 1.9 Ga Pechenga Complex in Russia (Fiorentini *et al.*, 2008). The Archean and Early Proterozoic amphiboles, which have petrographic and textural features (*i.e.*, poikilitic texture) closely resembling those of igneous cumulates (hornblendites) from Phanerozoic arc settings, were thus considered for comparison. Furthermore, a series of amphibole megacrysts from southwest USA (Hoover Dam and Dish Hill) were also considered for comparison. In all the studied rocks, the crystallisation of amphibole follows that of the early crystallising minerals: olivine + spinel ± orthopyroxene + clinopyroxene. In Table 1 are summarised the petrological characteristics and ages of studied samples.

GEOCHEMICAL CHARACTERIZATION OF AMPHIBOLE

In situ major element concentrations in olivine, clinopyroxene and amphibole grains were analysed with a Jeol JXA - 8200 electron Super probe at the Università degli Studi di Milano, Milano (Italy). The microprobe is equipped with WDS and EDS. Operating conditions included a beam size of 5 µm and current of 20 nA, with an accelerating voltage of 15 kV. All data were obtained using WDS and counting times of 20 s on peak and 20 s on background. *In situ* trace element concentrations of olivine, clinopyroxene and amphibole grains were determined by laser ablation Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) at the Istituto di Geoscienze e Georisorse - Consiglio Nazionale delle Ricerche (IGG-CNR), Pavia (Italy). The instrument couples a 266 nm Nd:YAG laser microprobe (Brilliant, Quantel) to a quadrupole ICP-MS system (DRCe from PerkinElmer). NIST-SRM612 was used as an external standard, whereas ^{43}Ca or ^{29}Si were adopted as internal standards, depending on the analysed mineral. In each analytical run the USGS reference sample BCR2 was analysed together with the unknowns for quality control. Precision and accuracy were better than 5% and 10%, respectively.

Table 1 - Summary of the petrography and ages of the selected samples. The ages are from literature: Garcia *et al.*, 1980; Stone *et al.*, 2003; Fiorentini *et al.*, 2008; Tiepolo & Tribuzio 2008; Fiorentini & Garwin 2010; Fiorentini *et al.*, 2012; Tiepolo *et al.*, 2014; Esna Ashari *et al.*, 2016.

	Locality	Rock type	Main assemblage	Accessory minerals	Age
Australia Agnew-Wiluna GB	Mt. Keith	Pyroxenite	pyroxene - brown amph	olivine - sulphides spinel	2.7 Ga
	Mt. Clifford	Pyroxenite	olivine - pyroxene	brown amph - Cr-spinel brown mica -magnetite	2.7 Ga
Canada Abitibi GB	Theo's Flow	Peridotite	clinopyroxene	brown amph - Cr-spinel magnetite - sulphides	2.7 Ga
	Boston Creek	Peridotite	olivine - clinopyroxene	brown amph - Cr-spinel magnetite - talc chlorite - tremolite	2.7 Ga
	Ghost Range	Peridotites	olivine - clinopyroxene orthopyroxene	brown amph - brown mica Cr-spinel	2.7 Ga
Russia Pechenga Complex	Pilgüjarvi sill	Peridotites	olivine - clinopyroxene	brown amph - brown mica magnetite - sulphides	1.98 Ga
		Magnetite-peridotite	magnetite - ilmenite olivine	clinopyroxene -sulphides brown amph - brown mica	1.98 Ga
	Kammikivi sill	Peridotite	olivine - clinopyroxene	brown amph - brown mica Cr-spinel - magnetite	1.98 Ga
	Nyasyukka dike complex	Peridotites	olivine - brown amph clinopyroxene	brown mica - plagioclase magnetite - sulphides ilmenite	1.96 Ga
Antarctica Ross Orogen	Husky Ridge	Qtz-diorite	brown amph - green amph plagioclase	clinopyroxene brown mica - qtz titanite - sulphides	512 Ma
Italy Alps Orogen	Mt. Mattoni	Hornblendites	brown amph - olivine	clinopyroxene green amph - magnetite sulphides	40 Ma
	Val Masino	Hornblendite	brown amph-clinopyroxene olivine	green amph - magnetite sulphides	30 Ma
Japan Japan Arc	Taku	Gabbrodiorite	brown amph - green amph clinopyroxene - orthopyroxene olivine	plagioclase - sulphides Fe-oxides	120 Ma
	Zenifudo	Hornblendite	brown amph - clinopyroxene orthopyroxene - olivine green amph - plagioclase	brown mica - Fe-oxides	76 Ma
	Hase no Yatsu	Hornblendite	brown amph - clinopyroxene orthopyroxene - olivine green amph	brown mica - Fe-oxides	117 Ma
Tibet Himalayan Orogen	Gangdese batholith	Hornblendites	brown amph - green amph clinopyroxene	brown mica - Fe-oxides	82 Ma
Iran Zagros Orogen	Sanandaj-Sirjan Zone; Aligoodarz pluton	Olivine-hornblende Pyroxenite	brown amph - clinopyroxene orthopyroxene - olivine	brown mica - spinel sulphides	165 Ma
Indonesia Sunda arc	Batu Hijau district Sumbawa	Porphyritic hornblende Tonalite	plagioclase - brown amph qtz	Fe-oxides	4.9 Ma
USA	Hoover Dam	Alkali amphibole megacrysts	brown amphibole		2-3 Ma
	Dish Hill	Alkali amphibole megacrysts	brown amphibole		2-3 Ma

The samples were prepared for *in situ* secondary ions mass spectrometry (SIMS) analysis at the Università degli Studi di Milano and at the IGG-CNR of Pavia. The Precambrian amphibole grains most suitable for the analysis were selected on the polished thin sections and then drilled out in the form of a core of 2 mm-diameter. The cores were cleaned with acetone and embedded in indium mount. For the in mount preparation the procedure described by the SIMS laboratory of the University of Edinburgh was followed. Igneous amphiboles were analysed *in situ* for δD and $\delta^{18}O$ ratio with a CAMECA IMS 1270 E7 ion microprobe at the Centre de Recherche Pétrographiques et Géochimiques-Centre National de la Recherche Scientifique CRPG-CNRS of Nancy (France). The spots for SIMS analysis were carried out on fresh amphibole grain surface, far from scratches. The analytical procedure is described in Deloule *et al.*, (1991). The H, F and Cl concentration were measured with the ion probe Cameca IMS 4f, at the CNR-Istituto di Geoscienze e Georisorse (IGG)-Unità di Pavia, following the method described in Gentili *et al.*, (2015).

RESULTS AND DISCUSSION

The Precambrian rocks considered in this work share many petrographic and textural similarities with hornblendites and amphibole-bearing pyroxenites from Phanerozoic orogenic settings. However, chemical compositions of Precambrian amphiboles are more comparable with those characterising amphibole megacrysts from alkaline lavas as shown in Fig. 1. In the Archean and Early Proterozoic samples at first the origin of amphibole was constrained. The geobarometric calculations reveal large uncertainty on crystallisation pressures. The Al-in amphibole geobarometric calculations reveal a crystallisation P for amphibole > 3 kbar (at depth > 9.9 km, estimates using a geobarometric gradient of 3.3 km/1 kbar; Hagemann and Brown, 1996). For few localities, these P estimates are confirmed also by the application of the geobarometer of Putirka (2016), thus suggesting their reliability. Others localities yield negative pressure estimates pointing to very low P crystallization conditions of amphibole.
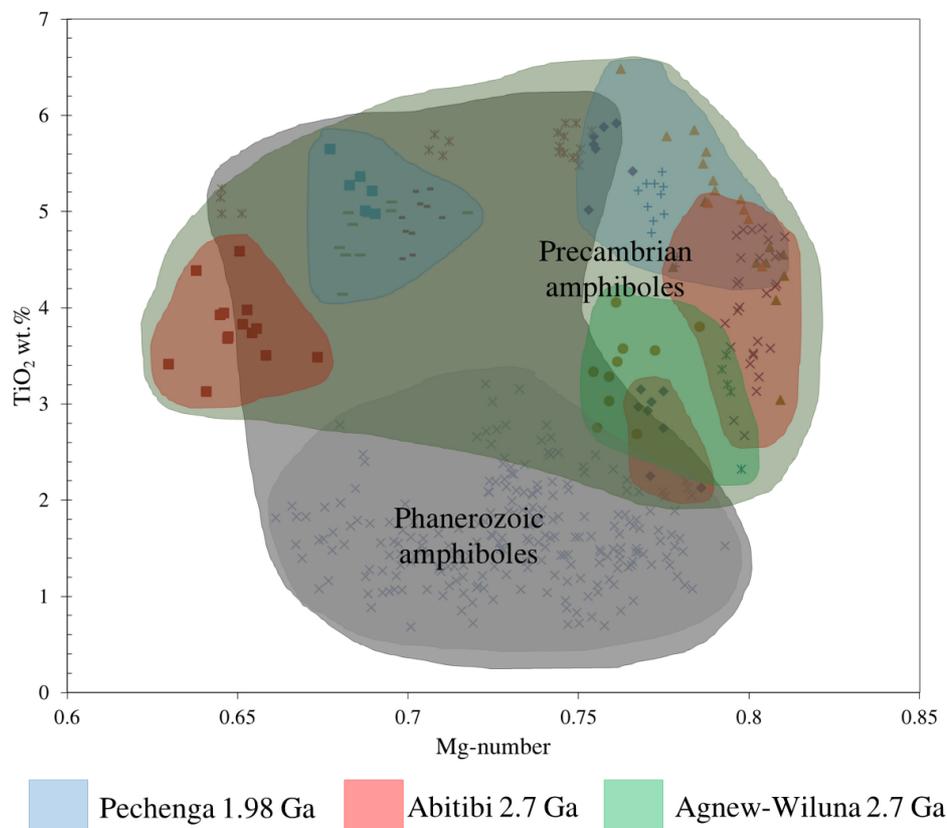

Fig. 1 - Mg-number *versus* TiO_2 wt.% in the studied amphiboles.

In order to understand the significance of amphibole in rocks that should be virtually anhydrous, the equilibrium between amphibole and primary clinopyroxene was tested using a textural and geochemical approach based on the Fe-Mg and REE partitioning. The amphibole-bearing rock from the Abitibi Greenstone Belt are those in which amphibole is apparently most far from equilibrium with the associated clinopyroxene (Fig. 2). In the amphibole-bearing rock from the Pechenga Complex (Pilgüjarvi and Kammikivi sills) amphibole and clinopyroxene are instead very close to equilibrium conditions. Amphibole crystallisation in most of the studied rocks seems to occur from a more differentiated melt, *i.e.* with low Mg-number and enriched in REE (LREE over HREE in particular). Furthermore, Precambrian amphiboles are Ni-enriched compared to associated clinopyroxene, suggesting that amphibole has assimilated Ni-rich precursor phases (*e.g.*, olivine). These evidences of disequilibrium between amphibole and clinopyroxene suggests that amphibole did not crystallised "on site" from the same melt of the clinopyroxene. Two different scenarios were proposed to explain this disequilibrium: *i*) amphibole and clinopyroxene have the same parental liquid that evolved in closed system becoming rich in water by fractional crystallisation of anhydrous phases until the stability of amphibole is reached; *ii*) H_2O-rich melts have percolated the cumulate pile reacting with clinopyroxene and inducing amphibole crystallisation.
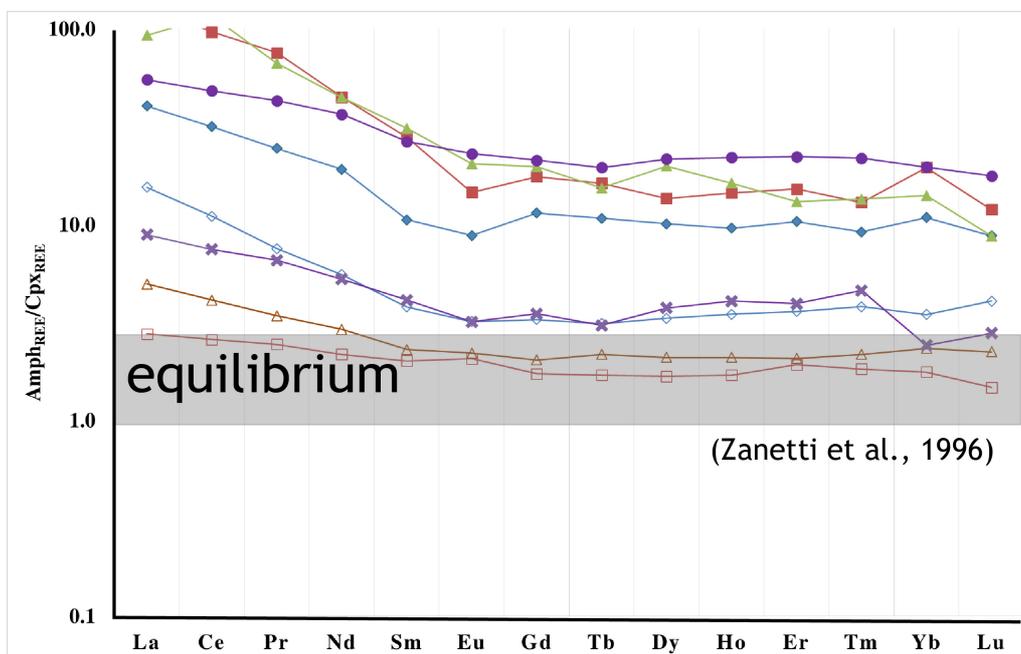

Fig. 2 - Amph/Cpx DREE pattern for the Precambrian samples. Amph/cpx equilibrium range from Zanetti *et al*. (1996).

In order to constrain which of these hypotheses are the most reliable, a model of fractional crystallisation was carried out considering the bulk compositions of the studied rocks and evolving the melt by crystallisation of the early cumulus minerals (olivine, orthopyroxene and clinopyroxene). The crystallisation model shows that the measured amphibole REE composition can be obtained in all localities (with the exception for Canada samples) by differentiation of the primary melt by fractional crystallisation of the early cumulus minerals, thus implying that a completely external melt is not required. For the Canadian localities, the model fails to reproduce the strong LREE enrichment and a LREE exotic component may be taken into account. My conclusion is that amphibole in the Archean and Early Proterozoic rocks crystallized from a melt likely evolved by fractional crystallisation from the primary melt. The disequilibrium between amphibole and clinopyroxene highlights that amphibole crystallisation likely occurred during melt migration within the cumulate pile. Other evidences denote that fractional crystallisation is however not the only differentiation process recorded by amphibole. The distribution of the transition metals in amphibole and clinopyroxene supports the hypothesis that amphibole crystallisation follows a melt/rock reaction process between a primary assemblage (likely, olivine +

magnetite/ilmenite + clinopyroxene) and a melt (likely, more evolved) that promoted the partial reabsorption of the primocrystic phases and induced the mobilisation of Ni (from olivine) and Cr (from pyroxene).

      Another step towards the understanding of the significance of amphibole in rocks that should be virtually anhydrous is to constrain the origin of water. In particular, the origin of amphibole from the hydration of the cumulate pile (in particular of clinopyroxene) in response to the circulation of seawater-derived fluids cannot be also a priori excluded. Proxies for this process are fluid-mobile elements such as Cl, F, Ba, B and Sr. As shown in Fig. 3, the Archean and early Proterozoic amphiboles do not fall in any of the known magmatic and hydrothermal fields. They have Nb/La ratios falling in the magmatic amphiboles field whereas the Cl/F ratios are higher and comparable with those of hydrothermal amphiboles. The shift toward high Cl/F ratio, at constant Nb/La ratios, can be however likely related to the F depletion induced in the melt by fractional crystallisation of amphibole itself. However, it cannot be excluded that the high Cl/F ratios is a primary feature of the mantle sources. The Archean and early Proterozoic amphiboles are also Sr-enriched and, generally, B-depleted. All these features thus suggest that a contribution of seawater-derived fluid is unlikely.
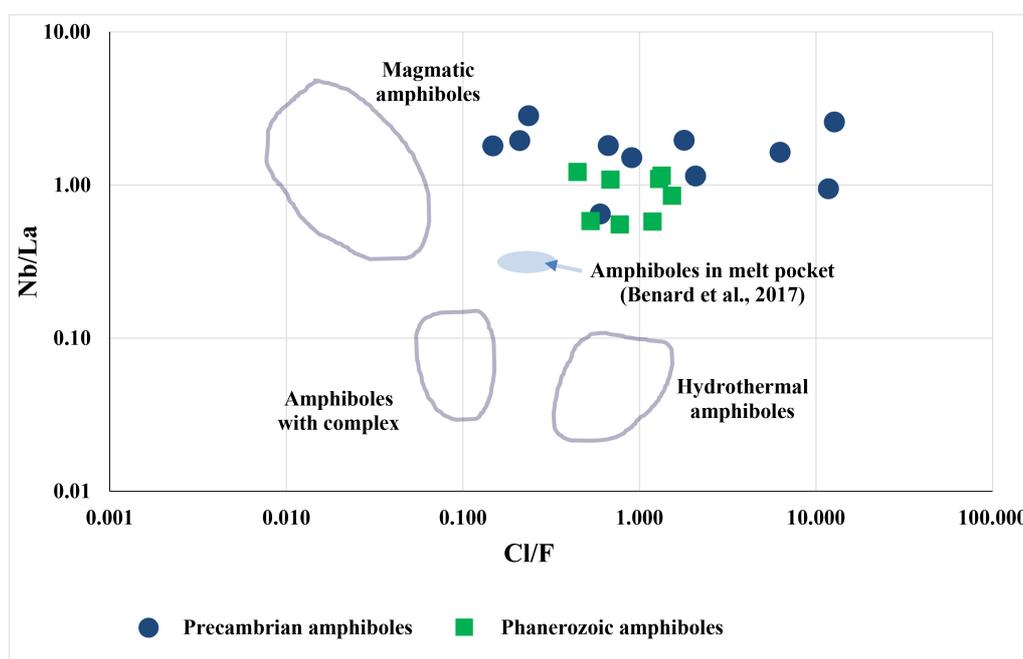

Fig. 3 - The ratio Cl/F versus Nb/La of Precambrian and Phanerozoic amphiboles is reported. The amphibole compositional fields are those from Coogan *et al.* (2001) for magmatic and hydrothermal amphiboles in a suite of gabbros from the Mid-Atlantic Ridge.

      The H_2O concentrations (Fig. 4) in the Archean and early Proterozoic amphiboles are comparable to those of either subduction related or amphibole megacrysts of alkaline lavas. A common feature is also a not full occupancy of the $^{O3}O^{2-}$ structural crystalline site of the amphibole, typical of all high temperature igneous amphiboles. To constrain the origin of water in amphibole the δD and δ^{18}O were determined *in situ* by ion microprobe (*e.g.*, SIMS technique). The range of δD values (Fig. 5) of the Archean and Paleoproterozoic amphiboles ranges between -99.5‰ and -129.8‰, that is slightly lower if compared to the mantle range but still consistent with a magmatic origin for water. This δD signature is thus also in contrast with an origin of amphibole by hydration of the cumulate minerals by seawater fluids, as proposed by their Cl/F ratios and Sr-B budgets. However, the hypothesis of a crustal contribution in the origin of the amphiboles, and in turn a non-mantellic origin of water, seems supported by the oxygen isotope signature of amphibole. All amphiboles show δ^{18}O values lighter (between 2.5 ± 0.42 ‰ and 5.0 ± 0.30‰) than those of the mantle with the sole exception (6.4 ± 0.99 ‰) of the olivine-magnetite peridotite from the Pechenga Complex (for which a small crustal input is thus not excluded). The light δ^{18}O values of amphiboles in Archean and early Proterozoic rocks could be ascribed to the interaction of the amphibole parental melts with recycled altered oceanic materials, which are the

most suitable input of seawater-like geochemical anomalies into the mantle during time. Nevertheless, this is unlikely because fluid-mobile elements and hydrogen isotopes have already suggested that seawater apparently was not involved in the petrogenesis of the studied amphiboles. Furthermore, the oxygen isotope does not show any correlation with the seawater proxies (*e.g.*, B, Cl).
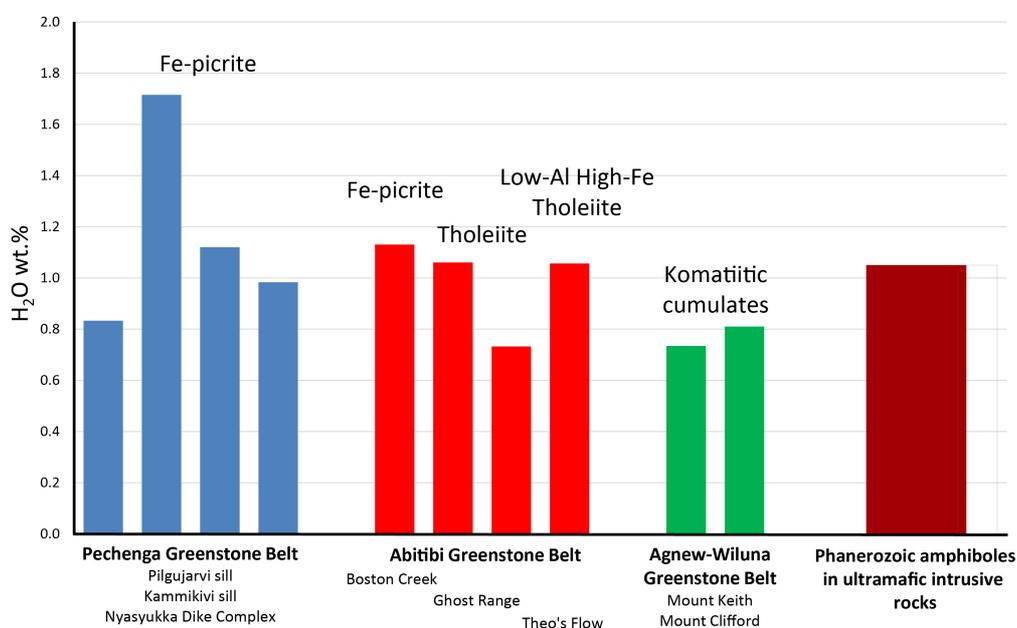

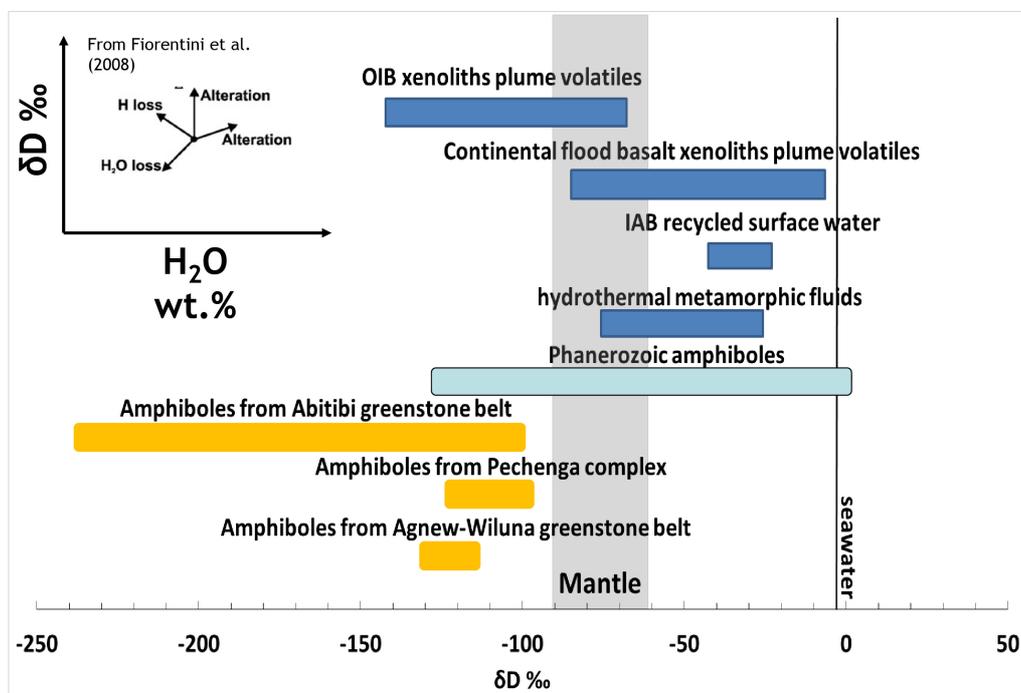Fig. 4 - Water contents analyzed in Precambrian and Phanerozoic amphiboles.

Fig. 5 - The hydrogen isotopic data and water contents of Precambrian and Phanerozoic amphiboles. The modern xenoliths, vent fluids, mantle field and seawater δD values are from Deloule *et al.* (1991) and Shaw *et al.* (2008).

All these geochemical evidences pointed out that the light $\delta^{18}O$ signature of most of the Archean and Paleoproterozoic amphiboles is likely a primary feature of the mantle source. Further evidence of mantle

composition heterogeneity are observed in anomalously enriched Nb/Ta signature that occurs in some of the investigated magmas spanning in space and time throughout the complex evolution of the planet has to be a primary feature of their mantle sources. These new data are inconsistent with the interpretation of a secular homogeneity of the subchondritic Nb/Ta signature of the silicate Earth (*e.g.*, Munker *et al.*, 2003). Conversely, the observed heterogeneous Nb/Ta signature of the Earth's silicate mantle resulted from the complex assembly of non-homogeneous geochemical reservoirs over a protracted geological time. The tapping of anomalously enriched mantle domains throughout the entire evolution of the planet, since the early Archean through to the Phanerozoic, implies that some "early" moon-like deep mantle domains (the source of the early Archean komatiites) escaped complete equilibration with the subchondritic Earth's mantle and reached the shallower source of the Phanerozoic melts. However, any inference on the abundance of these enriched domains in the Earth's mantle is speculative due to the paucity of samples so far considered.

All studied amphiboles are in equilibrium with melts resembling the alkaline affinity of the primary melt that has been suggested in the literature for the different igneous complexes. The incompatible trace element pattern parallels at higher values that of modern OIB (with respect to MORB and IAB) even if display negative Sr and Ti anomalies (Fig. 6).
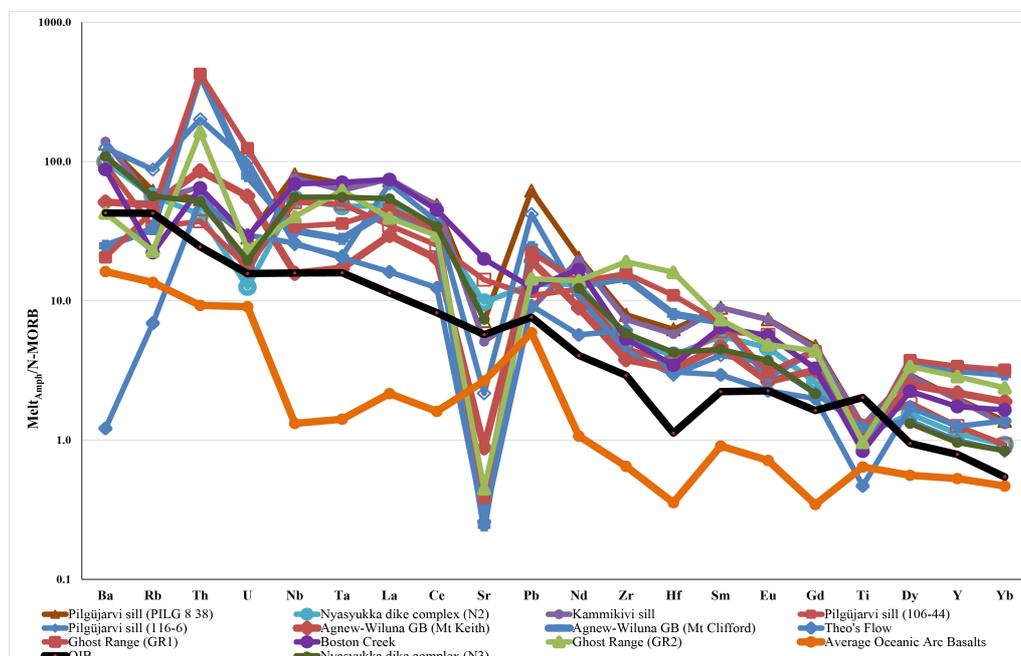

Fig. 6 - The N-MORB normalized incompatible trace element patterns for the calculated melts in equilibrium with Precambrian amphiboles. The data of MORB, OIB and IAB compositions are from McDonough & Sun (1995) and Kelemen *et al.* (2003), respectively.

This higher overall incompatible trace element values with respect present day OIB can be easily interpreted as the result of melt differentiation prior the crystallisation of amphibole. Sr and Ti anomalies are likely related to the crystallisation of mineral phases with a high compatibility for Sr and Ti such as amphibole itself or phlogopite. In order to constrain the fO_2 condition of the late Archean-early Proterozoic mantle, the Sc and V concentrations in primary melts were calculated for Precambrian and Phanerozoic samples by applying amphibole/melt partition coefficient for Sc and V. The calculated melts are characterized by relatively homogeneous Sc/V ratios, except for the Australian komatiite of Mt. Clifford and the Canadian Fe-picrite of Boston Creek that have exceptionally low Sc/V ratios (0.04-0.10). Sc/V ratios of Archean and early Proterozoic melts are almost comparable with those of amphibole megacrysts from alkali lavas (Sc/V = 0.15), thus suggesting that the oxygen fugacity conditions of the mantle source in the Archean and early Proterozoic were similar to those of alkaline lavas during Phanerozoic. Noteworthy is that for similar geodynamic settings

amphiboles of the present study do not show any significant variation in the oxygen fugacity conditions from Archean to Phanerozoic. The lower Sc/V ratios characterising Archean and early Proterozoic amphiboles with respect to Phanerozoic arc-related melts is a further evidence that in the Archean and early Proterozoic there is no evidence of a subduction-related component in the source of mafic melts (at least those having amphibole as a late crystallising mineral).

CONCLUSION

A main conclusion of this work based on the comparison of the water content in primary melts from Archean-early Proterozoic amphiboles and present-day OIB, MORB and IAB is that the Archean mantle source of the komatiites had a much higher water content than that characterizing present day OIB. This is in agreement with the finding that the high-pressure polymorphs of olivine could have exceptionally high concentrations of H_2O and F, (and possibly Cl) thus representing a good volatile-reservoir in the deep mantle. Conclusions about tholeiites are more problematic. The fractionated trace element pattern of these melts, paralleling that of OIB, suggests that the mantle source was relatively enriched in incompatible elements even if the water content is low and similar to that of present-day N-MORB. These contrasting features may reflect local heterogeneities of the mantle or different depths (shallower) at which partial melting has occurred. The early Proterozoic Fe-picrites yield an incompatible trace element patterns resembling that of modern OIB but with highly variable water contents suggesting a large heterogeneity in the water composition of the mantle source. Heterogeneity of the mantle through the Earth's history was also observed for the Nb/Ta signature. Some of the calculated melts (since early Proterozoic) show an enriched Nb/Ta signature that is independent from space (geological setting) and time and that was interpreted as a primary feature of the different mantle sources. The observed heterogeneous Nb/Ta signature of the Earth's mantle was interpreted as related to the addition of extra-terrestrial material after the mantle-core equilibration and prior 4.4 Ga and to a not complete equilibration of these domains during the Earth's evolution.

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