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Al-free di-trioctahedral substitution in chlorite and a ferri-sudoite end-member

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ABSTRACT: A compilation of Fe^{3+}-bearing chlorite analyses is used: (1) to investigate the Al-free di-trioctahedral (AFDT) substitution $2Fe^{3+} + \square = 3(Mg,Fe^{2+})$ in chlorite; and (2) to estimate the composition of a ferri-sudoite end-member $(Si_3Al)[(Fe^{2+},Mg)_2Fe_2^{3+}\square Al]O_{10}(OH)_8$ within the chlorite solid-solution domain. According to our observations, up to two Fe^{3+} cations might be allocated in the M2-M3 chlorite sites by the substitution AFDT, which does not involve Al. These unexpected observations were made possible by the development of µXANES techniques allowing *in situ* measurements of XFe^{3+} ($Fe^{3+}/(Fe^{2+} + Fe^{3+})$) in heterogeneous chlorite. Although further studies are required to confirm the crystallographic position of Fe^{3+} and refine its ionic/magnetic behaviour in chlorite, this development creates opportunities for developing new geothermometers.

KEYWORDS: chlorite, µXANES, geothermometry, sudoite.

Chlorite is a ubiquitous phyllosilicate composed of tetrahedral and octahedral layers according to the 14.2 Å 2:1:1 arrangement (*e.g.* Meunier, 2005). The tetrahedral sheet hosts tri- or tetravalent cations (Si^{4+}, Al^{3+} or rarely Ti^{4+}, Fe^{3+}), while the octahedral one is composed of di- or trivalent cations (usually Fe^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+} and Fe^{3+}). The general formula of chlorite is: $R^{2+}_{6-x-3y}R^{3+}_{x+2y}\square_y(Si_{4-x}R^{3+}_x)O_{10}(OH)_8$, in which R^{2+} represents divalent cations, R^{3+} trivalent cations and $\square$ octahedral vacancies (*e.g.* Wiewióra & Weiss, 1990). According to Bailey (1988), the chlorite structure is formed of two types of tetrahedral crystallographic sites (denoted T1 and T2) and two octahedral sites (denoted M1 and M2). Two other octahedral sites (M3 and M4) are located in the brucite interlayer space. Al^{VI} or trivalent Fe^{3+} cations are located preferentially in the M4 site, while the divalent cations occupy the other sites (Bailey, 1988). There are three categories of chlorite in diagenetic and low- to high-grade metamorphic rocks: tri-trioctahedral (sum of octahedral cations close to 6 a.p.f.u), di-trioctahedral (5 a.p.f.u) and di-dioctahedral (4 a.p.f.u). The main chemical substitutions occurring in chlorite are: Tschermak (TK) $Si^{4+}_{(IV)} + (Fe^{2+}, Mg^{2+})_{(VI)} = Al^{3+}_{(IV)} + Al^{3+}_{(VI)}$; ferromagnesian (FM) $Mg^{2+}_{(VI)} = Fe^{2+}_{(VI)}$ and di-trioctahedral (DT) $2Al^{3+}_{(VI)} + \square_{(VI)} = 3(Mg^{2+},Fe^{2+})_{(VI)}$. Two filling models are used in the literature for the distribution of cations on the crystallographic sites. The first model referred to as 'disorderly', considers that there is no preferred configuration (*e.g.* Inoue *et al.*, 2009). The second model, referred to as 'ordered' is constrained by specific rules for filling cations in the crystallographic sites such as preferred configuration and Fe-Mg equipartition (*e.g.* Vidal *et al.*, 2001, 2005, 2006; Lanari *et al.*, 2014a). These authors assume, following Holland *et al.* (1998), Al_{IV} in T2, vacancies in M1, Al_{VI}

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TABLE 1. Structural formulae for classic chlorite end-members and the new ferri-sudoite end-member.

	T1(2)	T2(2)	M1(1)	M2-M3(4)	M4(1)
Amesite-Mg/corundophilite	Si,Si	Al,Al	Al	Mg,Mg,Mg,Mg	Al
Amesite-Fe	Si,Si	Al,Al	Al	Fe,Fe,Fe,Fe	Al
Clinochlore	Si,Si	Si,Al	Mg	Mg,Mg,Mg,Mg	Al
Chamosite/daphnite	Si,Si	Si,Al	Fe	Fe,Fe,Fe,Fe	Al
Sudoite-Mg	Si,Si	Si,Al	□	Mg,Mg,Al,Al	Al
Sudoite-Fe	Si,Si	Si,Al	□	Fe,Fe,Al,Al	Al
Al-free chlorite	Si,Si	Si,Si	Mg	Mg,Mg,Mg,Mg	Mg
Pyrophyllite-gibbsite	Si,Si	Si,Si	□	Al,Al,Al,□	Al
Ferri-sudoite	Si,Si	Si,Al	□	$(Fe,Mg)_2,Fe^{3+},Fe^{3+}$	Al

The numbers in parentheses refer to the quantity of atoms (per structural formula) distributed in tetrahedral (T) or octahedral (M) sites.

in M4 then M1 and then, eventually, in M2-M3, Fe and Mg in M2-M3 then in M1. Following the equipartition assumption, *X*Mg ($Mg^{2+}/(Mg^{2+}+Fe^{2+})$) is considered to be equal between the M1 and M2-M3 sites. Several chlorite end-members are classically defined (Table 1): Al-free chlorite $(Si_4)[Mg_6]O_{10}(OH)_8$, amesite $(Si_2Al_2)[(Fe^{2+},Mg)_4Al_2]O_{10}(OH)_8$, clinochlore $(Si_3Al)[Mg_5Al)O_{10}(OH)_8$, corundophilite $(Si_2Al_2)[Mg_4Al_2]O_{10}(OH)_8$, daphnite $(Si_3Al)[Fe^{2+}_5Al]O_{10}(OH)_8$, pyrophyllite-gibbsite $(Si_4)[Al_4\square_2]O_{10}(OH)_8$ and sudoite $(Si_3Al)[(Fe^{2+},Mg)_2\square Al_3]O_{10}(OH)_8$. These end-members do not include any ferric iron component.

For 15 years, many authors have emphasized the importance of Fe^{3+} in chlorite, particularly in terms of its use as a geothermometer (Laird, 1988; Vidal *et al*., 2006; Inoue *et al*., 2009; Bourdelle *et al*., 2013; Lanari *et al*., 2014a). An additional substitution: Al-Fe^{3+} that is supposed to occur on the M4 site was defined but without defining a ferric chlorite end-member (Vidal *et al*., 2006). In this model, the incorporation of Fe^{3+} changes the chlorite composition and the activity of the other end-members. This choice of the M4 site is based on the results of Smyth *et al*. (1997) suggesting that Fe^{3+} in chlorite shows a strong preference for the M4 site where it substitutes for Al^{3+}.

Several methods are available to measure Fe^{3+} in chlorite: chemical titration (Tschermak, 1891; Orcel, 1927; Hallimond *et al*., 1939; Brindley, 1951), Mössbauer (Pal *et al*., 1993; Aja & Dyar, 2000; Inoue *et al*., 2009), X-ray photoelectron spectroscopy (XPS) (Inoue *et al*., 2010) and micro-X-ray absorption near-edge spectroscopy (μ-XANES) (Wilke *et al*., 2001; Vidal *et al*., 2006; Rigault, 2010; Trincal *et al*., 2015).

CHLORITE DATA FROM THE LITERATURE

A compilation of almost 200 published data of chlorite structural formulae containing Fe^{3+} is reported in Table 2. These chlorites come from a wide range of rocks from various localities. Some are of detrital origin; another experienced diagenetic to metamorphic conditions as indicated by the oscillatory zoned chlorites from the Pic-de-Port-Vieux outcrop (Fig. 1; Trincal *et al*., 2015). In addition, 202 data from three localities were incorporated in this review (Inoue *et al*., 2009). Most of the chlorites selected contain (in a.p.f.u, see Table 2): 2.5 to 3.5 Si^{4+}, 2 to 4 Al^{3+} (Fig. 2), 1.5 to 5.5 R^{2+} (Mg^{2+}, Mn^{2+}, Fe^{2+}) (Fig. 3) and <1 Fe^{3+} (Fig. 4). These analyses are distributed between classical end-members and apparently follow the classical DT and TK substitutions (Figs 2, 3) or the Al-Fe^{3+} substitution (Fig. 4).

In diagenetic to metamorphic rocks, the XFe^{3+} content of chlorite depends on the temperature and the oxygen fugacity that is controlled by the buffering assemblage, *i.e.* the bulk-rock composition (Lanari *et al.* 2014a). This control is supported by data from Inoue *et al.* (2009), which show relationships between sampling localities and chlorite structural formulae and oxidation state (Figs 2–4). It is therefore critical to look at the variability of XFe^{3+} recorded by chlorite in one rock sample, for a given bulk-rock composition. In such cases the observed variability of XFe^{3+} is caused by temperature variations,

TABLE 2. Compilation of structural formulae for Fe^{3+}-bearing chlorites, calculated on the basis of O = 14.

N°	Reference	Method	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	MnO	CaO + Na_2O + K_2O	Others	Total	Si	Ti	^{IV}Al	^{VI}Al	Fe^{3+}	Fe^{2+}	Mg	Mn	□
1	Trincal *et al*. (2015)	XAN	25.17	0.01	22.76		20.98	17.27	0.09	0.05	0.05	86.37	2.58		1.42	1.33	0.68	1.04	2.64		0.30
2	Trincal *et al*. (2015)	XAN	26.11	0.01	22.93		18.43	19.64	0.09	0.04	0.05	87.29	2.63		1.37	1.35	0.38	1.13	2.95		0.18
3	Trincal *et al*. (2015)	XAN	25.74	0.01	23.25		20.43	17.86	0.09	0.04	0.05	87.47	2.60		1.40	1.37	0.53	1.14	2.69		0.25
4	Trincal *et al*. (2015)	XAN	25.98	0.01	23.65		18.39	19.09	0.09	0.04	0.05	87.30	2.62		1.38	1.42	0.32	1.19	2.87		0.18
5	Trincal *et al*. (2015)	XAN	25.53	0.01	23.16		21.94	16.41	0.08	0.04	0.04	87.23	2.59		1.41	1.37	0.74	1.04	2.48		0.35
6	Trincal *et al*. (2015)	XAN	25.76	0.02	22.91		21.92	16.36	0.10	0.05	0.05	87.17	2.62		1.38	1.37	0.70	1.08	2.48		0.35
7	Trincal *et al*. (2015)	XAN	26.39	0.01	23.00		17.59	19.83	0.11	0.05	0.05	87.02	2.65		1.35	1.38	0.36	1.08	2.97		0.20
8	Trincal *et al*. (2015)	XAN	25.75	0.02	23.17		20.47	17.44	0.11	0.05	0.05	87.04	2.62		1.38	1.39	0.53	1.15	2.64		0.27
9	Trincal *et al*. (2015)	XAN	25.85	0.01	23.55		18.70	18.83	0.11	0.05	0.05	87.15	2.61		1.39	1.42	0.33	1.22	2.84		0.18
10	Trincal *et al*. (2015)	XAN	25.55	0.02	23.05		21.48	16.58	0.11	0.05	0.05	86.87	2.60		1.40	1.37	0.72	1.02	2.52		0.35
11	Debret *et al*. (2015)	XAN	33.76		12.69		4.17	33.65			1.59	86.14	3.23		0.77	0.66	0.20	0.14	4.80		0.04
12	Debret *et al*. (2015)	XAN	33.73		13.54		3.35	33.92			1.40	87.00	3.19		0.81	0.70	0.17	0.16	4.79		0.03
13	Debret *et al*. (2015)	XAN	33.47		13.24		3.26	33.66			1.76	85.57	3.21		0.79	0.71	0.13	0.13	4.81		0.02
14	Zhang *et al*. (2011)	CHE											2.67	0.01	1.33	1.24	0.47	1.51	2.75	0.01	0.19
15	Inoue *et al*. (2010)	XPS	29.98		15.56	6.36	16.45	16.68	0.40	0.33		85.75	3.13		0.87	1.05	0.50	1.44	2.60	0.04	0.33
16	Inoue *et al*. (2010)	XPS	28.08	0.07	18.34	3.80	13.82	19.08	1.12	0.31		84.60	2.93	0.01	1.07	1.18	0.30	1.21	2.97	0.10	0.19
17	Inoue *et al*. (2010)	XPS	27.34	0.03	18.58	4.51	16.42	17.75	0.35	0.27		85.24	2.87	0.00	1.13	1.17	0.36	1.44	2.78	0.03	0.18
18	Inoue *et al*. (2010)	XPS	29.98	0.04	19.05	3.91	11.26	20.30	0.60	0.29		84.45	3.03	0.00	0.97	1.30	0.30	0.95	3.06	0.05	0.30
19	Inoue *et al*. (2010)	XPS	24.26	0.01	17.64	5.56	33.82	1.37	3.34	0.11		86.09	2.85	0.00	1.15	1.29	0.49	3.32	0.24	0.33	0.31
20	Inoue *et al*. (2010)	XPS	27.17	0.05	18.77	3.76	19.37	13.71	3.21	0.24		86.29	2.89	0.00	1.11	1.25	0.30	1.73	2.18	0.29	0.21
21	Inoue *et al*. (2010)	XPS	22.86	0.03	17.55	6.40	30.55	1.92	2.15	0.13		81.59	2.80	0.00	1.20	1.33	0.59	3.13	0.35	0.22	0.35
22	Rigault (2010)	XAN											2.63	0.01	1.36	1.41	0.13	2.51	1.84	0.01	0.08
23	Rigault (2010)	XAN											2.71		1.29	1.60	0.14	2.58	1.40	0.05	0.22
24	Rigault (2010)	XAN											2.92		1.08	1.62	0.10	1.82	2.11	0.02	0.31
25	Rigault (2010)	XAN											2.86		1.14	1.44	0.34	0.34	3.54		0.32
26	Rigault (2010)	XAN											2.78	0.01	1.21	1.10	0.79	0.79	2.94	0.03	0.34
27	Rigault (2010)	XAN											2.57	0.01	1.42	1.29	0.75	1.84	1.79	0.01	0.30
28	Rigault (2010)	XAN											2.93		1.07	1.53	0.18	0.39	3.57		0.32
29	Singer *et al*. (2009)	EXA											2.67	0.03	1.31	0.33	1.74	1.51	2.22	0.01	0.38
30	Vidal *et al*. (2006)	XAN											2.76		1.24	1.37	0.49	2.14	1.62		0.31
31	Vidal *et al*. (2006)	XAN											2.72		1.28	1.32	0.43	2.11	1.85		0.24
32	Vidal *et al*. (2006)	XAN											2.71		1.29	1.31	0.14	2.58	1.84		0.07

(continued)

TABLE 2. (*contd.*)

N°	Reference	Method	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	MnO	$CaO + Na_2O + K_2O$	Others	Total	Si	Ti	^{IV}Al	^{VI}Al	Fe^{3+}	Fe^{2+}	Mg	Mn	□
33	Vidal *et al.* (2006)	XAN											2.69		1.31	1.31	0.14	2.60	1.82		0.07
34	Zazzi *et al.* (2006)	MÖS	30.70	0.25	22.90	1.42		31.10	0.01	<0.20	0.01		2.88		1.12	1.41	0.01	0.10	4.35		0.15
35	Zazzi *et al.* (2006)	MÖS	33.60	0.11	13.70	5.95		32.90	0.13	<0.74	0.01		3.24		0.76	0.78	0.13	0.30	4.73		0.07
36	Brandt *et al.* (2003)	CHE	26.15		21.13	5.93	17.20	17.73				88.14	2.67		1.33	1.21	0.46	1.47	2.70		0.17
37	Brandt *et al.* (2003)	CHE	26.83		21.64	6.07	13.30	20.67				88.51	2.67		1.33	1.21	0.45	1.11	3.07		0.17
38	Aja & Dyar (2002)	MÖS	29.64	0.04	23.93		37.94	8.11	0.29	0.05	0.01		2.82		1.19	1.49	0.30	2.72	1.15	0.03	0.30
39	Aja & Dyar (2002)	MÖS	33.90	0.06	23.77		8.33	33.80	0.04	0.10	0.01		2.83		1.17	1.17	0.07	0.50	4.20	0.01	0.03
40	Aja & Dyar (2002)	MÖS	26.73	1.92	20.21		41.25	7.00	0.29	1.49	1.11		2.63	0.14	1.23	1.11	0.28	3.08	1.03	0.03	0.08
41	Billaut *et al.* (2002)	MÖS	37.02		35.61	0.89		11.07	0.07	1.20			3.23		0.77	3.11	0.03	0.02	1.65		1.19
42	Billaut *et al.* (2002)	MÖS	36.70		33.04	3.74		11.04		0.65			3.32		0.68	2.93	0.15	0.13	1.58		1.20
43	Billaut *et al.* (2002)	MÖS	36.81		30.58	7.25		8.13	0.11	1.14			3.42		0.58	2.87	0.33	0.24	1.24	0.01	1.31
44	Bertoldi *et al.* (2001)	MÖS	22.46	0.06	19.29	4.70	37.20	2.87	0.07			86.65	2.62	0.01	1.38	1.28	0.41	3.63	0.50	0.01	0.16
45	Bertoldi *et al.* (2001)	MÖS	30.38	0.10	18.70	0.79	6.29	29.81	0.05			86.12	2.94	0.01	1.06	1.08	0.06	0.51	4.30	0.00	0.04
46	Lougear *et al.* (2000)	MÖS											2.68		1.32	1.18	0.18	1.95	2.68		0.02
47	Mitra & Bidyananda (2001)	MÖS	27.69	0.02	22.26		12.26	24.56	0.17	0.01	0.08	87.05	2.73	0.00	1.27	1.32	0.37	0.64	3.61	0.01	0.22
48	Mitra & Bidyananda (2001)	MÖS	26.74	0.06	21.77		11.72	24.36	0.17	0.01	0.17	85.00	2.70	0.01	1.29	1.31	0.37	0.62	3.67	0.02	0.19
49	Mitra & Bidyananda (2001)	MÖS	27.42	0.05	22.11		12.28	24.72	0.15	0.01	0.16	85.67	2.72	0.00	1.28	1.30	0.38	0.64	3.65	0.01	0.20
50	Smyth *et al.* (1997)	MÖS	31.68	0.05	17.13	1.34	1.62	34.76	0.08		0.05		2.99	0.00	1.01	0.89	0.10	0.13	4.88	0.01	0
51	Malmström *et al.* (1996)	MÖS											3.50		0.50	0.70	0.10	0.10	4.90		0.15
52	May *et al.* (1995)												3.00		1.00	0.90	0.10	0.10	4.90		0
53	Gregori & Mercader (1994)	CHE											3.12		0.88	1.69	0.64	1.03	2.17		0.73
54	Gregori & Mercader (1994)	CHE											3.01		0.99	0.49	0.29	0.50	4.20		0
55	Gregori & Mercader (1994)	CHE											2.76		1.24	2.01	0.12	0.70	3.30		0.45
56	Pal *et al.* (1993)	MÖS	27.69	0.02	22.26		12.26	24.56	0.17	0.01	0.08	87.05	2.73	0.00	1.27	1.32	0.38	0.63	3.61	0.01	0.21
57	Pal *et al.* (1993)	MÖS	26.74	0.06	21.77		11.72	24.36	0.17	0.01	0.17	85.00	2.70	0.00	1.29	1.30	0.37	0.62	3.67	0.01	0.19
58	Pal *et al.* (1993)	MÖS	27.42	0.05	22.11		12.28	24.72	0.15	0.01	0.16	86.90	2.71	0.00	1.29	1.30	0.38	0.64	3.65	0.01	0.19
59	Anceau (1992)	CHE	35.70		33.77	2.81	0.35	13.26	0.04		0.06	86.00	3.24		0.76	2.85	0.19	0.03	1.79		1.14
60	Kawano & Tomita (1991)		39.25	0.48	32.94	2.98		9.49		0.26	0.02		3.54	0.03	0.43	3.07	0.20		1.28		1.41
61	Chamberlain *et al.* (1989)		24.40		21.14		32.65	11.74	0.07				2.59		1.41	1.24	0.16	2.73	1.86	0.01	0
62	Joswig & Fuess (1990)												2.85		1.15	0.97	0.18	0.28	4.55		0.00
63	Zheng & Bailey (1989)												2.96		1.04	0.54	0.23	0.09	4.73		0
64	Ahn & Buseck (1988)												2.83		1.17	4.32	0.07				1.61
65	DeGrave *et al.* (1987)												2.88		1.12	1.32	0.23	2.07	2.16	0.05	0.22
66	DeGrave *et al.* (1987)												2.68		1.32	1.06	0.14	1.44	3.06	0.07	0
67	DeGrave *et al.* (1987)												2.64		1.36	0.85	0.32	1.82	3.10		0

68	DeGrave *et al.* (1987)												2.69		1.31	1.55		0.86	3.47		0.12
69	Rule & Bailey (1987)												2.62		1.38	1.28	0.14	1.16	2.96		0.02
70	Ballet *et al.* (1985)												2.64		1.36	1.08	0.92	2.75	0.93		0.32
71	Ballet *et al.* (1985)												2.97	0.35	0.68	1.85	0.33	2.41	0.83		0.75
72	Ballet *et al.* (1985)												2.68		1.32	1.18	0.18	1.95	2.69		0.02
73	Ballet *et al.* (1985)												3.00		1.00	0.96	0.14	0.48	4.30		0.05
74	Lin and Bailey (1985)	32.90	0.06	35.40	2.69		14.73	0.01	0.01		0.07		3.00		1.00	2.81	0.18		2.00		1.00
75	MacKenzie *et al.* (1983)	20.95		35.21		8.28	22.88		0.58			88.90	2.01		1.99	2.00		0.66	3.28		0.00
76	MacKenzie *et al.* (1983)	21.42	0.26	34.06	0.63	0.95	28.66		0.51			86.49	2.02	0.02	1.98	1.82	0.04	0.08	4.04		0
77	Borggaard *et al.* (1982)												2.68		1.32	1.17	0.18	1.95	2.69		0.02
78	Kittrick (1982)												2.97		1.03	1.44	0.07	0.99	3.24		0.24
79	Kittrick (1982)												2.97		1.03	1.44	0.07	0.99	3.24		0.24
80	Kittrick (1982)												2.99		1.01	1.39	0.21	0.57	3.52		0.30
81	Kittrick (1982)												2.47		1.53	1.60		3.29	1.05		0.04
82	Kittrick (1982)												2.84		1.16	1.75	0.12	2.61	1.16		0.36
83	Kodama *et al.* (1982)	33.55		22.62	2.51	15.74	25.58	–					2.91		1.09	1.23	0.16	1.14	3.31		0.15
84	Kodama *et al.* (1982)	25.89		19.85	12.61	30.57	4.77	6.31					2.61		1.39	0.96	0.95	2.57	0.72	0.54	0.26
85	Kodama *et al.* (1982)	30.66		22.69	14.58	25.48	5.50	1.09					2.89		1.11	1.42	1.04	2.01	0.77	0.09	0.67
86	Kramm (1980)	32.81	0.18	35.71	2.66	1.07	13.54	0.29	0.06				2.99	0.01	1.00	2.85	0.18	0.08	1.84	0.02	1.01
87	Kramm (1980)												3.03		0.97	2.86	0.14	0.14	1.89	0.03	1.01
88	Kramm (1980)												3.04		0.96	2.87	0.13	0.14	1.88	0.04	1.02
89	Phillips *et al.* (1980)	32.20	0.03	15.23		1.19	35.56				3.40		3.02		0.98	0.72	0.04	0.04	4.95		0
90	Phillips *et al.* (1980)	31.58	0.04	15.37		1.42	34.93				3.57		2.99		1.01	0.71	0.06	0.06	4.92		0
91	Goodman & Bain (1979)												2.85	0.09	1.07	1.26	0.08	0.26	4.24		0.14
92	Goodman & Bain (1979)												3.12		0.89	0.60	0.18	0.32	4.95		0
93	Goodman & Bain (1979)												2.81		1.20	1.01	3.02	0.64	0.79	0.33	1.42
94	Goodman & Bain (1979)												3.12		0.88	1.47	0.13	3.18	0.73	0.12	0.35
95	Fransolet & Bourguignon (1978)	33.06		35.74	2.74	0.24	14.09	0.28					3.01		0.99	2.84	0.19	0.02	1.91	0.02	1.02
96	Fransolet & Bourguignon (1978)	32.82		36.16	2.45	0.05	14.35	0.24					2.99		1.01	2.86	0.17		1.94	0.02	1.01
97	Sudo & Shimoda (1978)	34.36		38.34	0.49		10.21		0.25				3.12		0.88	3.29	0.03		1.39		1.16
98	Sudo & Shimoda (1978)	35.67	0.19	37.41	0.20	0.09	11.97	0.02	1.25				3.18	0.01	0.81	3.12	0.01	0.01	1.59		1.12
99	Alysheva *et al.* (1977)	33.71		37.95	2.74	2.40	12.08		1.49				2.97		1.03	2.90	0.18	0.17	1.58		1.03
100	Alysheva *et al.* (1977)	36.07		32.42	1.99		15.94		0.44				3.24		0.76	2.67	0.13		2.14		0.99
101	Alysheva *et al.* (1977)	33.83	0.34	31.80	0.27	0.37	18.86		2.42				3.04	0.03	0.93	2.43	0.03	0.04	2.50		0.77
102	Ericsson *et al.* (1977)												2.95		1.05	0.46	0.08	0.07	2.39		0
103	Ericsson *et al.* (1977)												2.82		1.19	0.55	0.53	1.59	2.60	0.04	0

(continued)

TABLE 2. (*contd.*)

N°	Reference	Method	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	MnO	CaO + Na_2O + K_2O	Others	Total	Si	Ti	^{IV}Al	^{VI}Al	Fe^{3+}	Fe^{2+}	Mg	Mn	□
104	Malysheva *et al.* (1977)												2.54		1.46	0.90	1.13	2.60	1.10		0.28
105	Spanu *et al.* (1977)												2.49		1.51	1.51	0.61	2.53	0.71	0.25	0.31
106	Spanu *et al.* (1977)												2.54	0.05	1.41	1.05	0.54	2.19	2.00	0.12	0.09
107	Spanu *et al.* (1977)												2.55		1.45	1.37	0.33	1.50	2.65	0.03	0.13
108	Tsukuki & Honda (1977)												3.19		0.81	3.13	0.01	0.01	1.60		1.13
109	Honda (1975)		34.36		38.84	0.49		10.21		0.85		85.75	3.12		0.88	3.29	0.03		1.38		1.16
110	Vrublevskaya *et al.* (1975)		38.26		44.28	1.31	0.48				2.00		3.42		0.58	4.08	0.09	0.04			1.79
111	Kimbara & Nagata (1974)		33.10	0.30	37.43	0.87		13.12		0.44		85.26	3.01	0.02	0.97	3.05	0.06		1.78		1.04
112	Kimbara & Sudo (1973)		29.45	0.20	20.14	4.08	18.69	14.93	0.36	1.59		89.34	2.97	0.02	1.02	1.36	0.31	1.58	2.24	0.03	0.27
113	Kimbara *et al.* (1973)		30.84	0.12	14.15	2.59	18.42	20.62	0.10	0.84		87.68	3.15	0.01	0.84	0.87	0.20	1.58	3.14	0.01	0.09
114	Post & Plummer (1972)		25.80		18.30	4.10	21.30	20.30				89.80	2.64		1.36	0.85	0.32	1.82	3.10		0
115	Post & Plummer (1972)		27.90		25.20		10.60	24.20				87.90	2.69		1.31	1.55		0.85	3.48		0.12
116	Post & Plummer (1972)		30.50		17.30	2.90	6.10	32.80				89.60	2.87		1.13	0.79	0.21	0.48	4.60		0
117	Post & Plummer (1972)		33.90		14.60	2.70	2.10	34.60				87.90	3.16		0.84	0.77	0.19	0.16	4.81		0.06
118	Aleksandrova *et al.* (1972)												3.14		0.86	4.10	0.04	0.01	0.08		1.64
119	deWaal (1970)		27.27		15.21	4.35	2.78	10.13	0.06	0.28	29.87	89.98	2.99		1.01	0.95	0.36	0.25	1.65	0.01	0.15
120	de Waal (1970)		27.27		15.21	4.35	2.78	10.13	0.06	0.38	29.87		2.98		1.02	0.95	0.36	0.25	1.65	0.01	0.14
121	Shimoda (1970)		32.72	0.03	20.28	1.00		24.47	0.06	2.22		80.78	3.24	0.00	0.76	1.61	0.07		3.61	0.01	0.44
122	Drits & Lazarenko (1967)		31.17		37.49	1.04	1.95	14.25		0.26			2.85		1.15	2.90	0.07	0.15	1.95		0.91
123	Gomes (1967)												3.45		0.55	3.96	0.02	0.02	0.04	0.01	1.72
124	Weaver *et al.* (1967)												2.66		1.34	1.74	0.02	3.68	0.42		0.21
125	Frenzel & Sehembra (1965)												3.43		0.57	2.70	0.09	0.04	1.97		1.11
126	Horikoshi (1965)		27.31	0.22	19.69	3.23	18.58	19.01	0.27	0.80		89.11	2.78	0.02	1.20	1.16	0.25	1.58	2.88	0.02	0.11
127	Hayashi & Oinuma (1964)		35.63		34.87	5.01	0.43	8.63	0.05	1.83		86.45	3.26		0.74	3.02	0.34	0.04	1.17		1.31
128	Tsukahara (1964)		39.01	0.47	32.15	0.90	0.10	10.14		2.16			3.56	0.03	0.41	3.05	0.06	0.01	1.37		1.25
129	Tsukahara (1964)		30.66		30.55	0.47		10.13		1.79			3.24		0.76	3.04	0.04		1.59		1.00
130	Banno (1964)		24.45	0.21	21.99	20.80	28.04	11.90	0.54	0.25		89.46	2.59	0.02	1.39	1.36	0.17	2.19	1.88	0.05	0.06
131	Caillère *et al.* (1962)												2.70		1.30	4.30	0.03	0.02			1.52
132	Brydon *et al.* (1961)	CHE											2.80	0.09	1.11	3.31	0.38		0.76		1.18
133	Bilgrami & Howie (1960)		28.32	0.09	19.03	1.19	14.85	23.72	0.09	0.63		87.92	2.83	0.01	1.17	1.06	0.09	1.24	3.53	0.01	0
134	Nakamura (1960)		21.34	0.21	20.73	5.20	40.17	0.99	0.89	0.04		89.57	2.46	0.02	1.52	1.30	0.45	3.87	0.17	0.09	0.12
135	Lapham (1958)		36.43		12.24	0.94	6.87	30.94	0.11	0.33	0.63	88.49	3.43		0.57	0.79	0.07	0.54	4.35	0.01	0.15
136	Shimane & Sudo (1958)		33.14	0.08	10.04	4.00	5.66	32.64		0.80		86.36	3.25	0.01	0.75	0.41	0.29	0.46	4.77		0
137	Shirozu (1958)		29.73		17.95	0.68	10.05	21.84	8.24			88.49	2.98		1.02	1.09	0.05	0.84	3.26	0.70	0.06
138	Shirozu (1958)		22.81		20.35	4.84	34.87	6.11	0.56	0.10			2.54		1.46	1.20	0.40	3.24	1.01	0.05	0.07

139	Shirozu (1958)	23.38		19.32	2.51	38.38	5.39	0.58			89.56	2.63		1.37	1.20	0.21	3.61	0.90	0.06	0.02
140	Shirozu (1958)	26.04		19.96	1.85	21.34	18.56	0.47			88.22	2.69		1.31	1.13	0.14	1.85	2.86	0.04	0
141	Shirozu (1958)	29.71		19.75	0.29	6.59	30.79	0.30			87.43	2.84		1.16	1.07	0.02	0.53	4.39	0.02	0
142	Shirozu (1958)	32.27		14.99	1.56	6.89	31.75	0.09			87.55	3.10		0.90	0.79	0.11	0.55	4.54	0.01	0.00
143	Battey (1956)	27.11	0.35	17.42	2.91	30.98	9.75		0.21		88.73	2.93	0.03	1.07	1.15	0.24	2.80	1.57		0.16
144	Frondel (1955)	29.94	0.16	13.77	10.46	20.96	10.71	0.18	1.34		87.52	3.19	0.01	0.81	0.92	0.84	1.87	1.70	0.02	0.45
145	Stone & Weiss (1955)	28.73	0.41	19.16	1.97	10.99	26.37	0.15	0.10		87.88	2.81	0.03	1.19	1.03	0.15	0.90	3.85	0.01	0
146	Brindley & Youell (1953)	22.47		21.82	0.22	37.24	2.57				84.32	2.65		1.35	1.68	0.02	3.67	0.45		0.18
147	Brindley & Youell (1953)	23.48		22.45	43.37	0.45	2.60				92.35	2.35		1.65	1.00	3.27	0.04	0.39		1.31
148	Ginzburg (1953)	33.40		47.47		0.71	0.20		0.54	3.12	85.44	3.07		0.93	4.22		0.05	0.03		1.64
149	Mathias (1952)	29.84	0.15	20.20	0.80	15.00	21.83	0.13	0.80	0.03	88.78	2.93	0.01	1.07	1.27	0.06	1.23	3.19	0.01	0.12
150	Brindley (1951)	22.03	3.63	22.91	0.46	36.68	1.91	0.04	0.18	0.26	88.77	2.47	0.31	1.53	1.50	0.04	3.44	0.32	0.00	0
151	Brindley (1951)											3.10		0.90	1.30	0.60	3.35	0.75		0.50
152	Brindley (1951)											2.48	0.30	1.22	1.82	0.04	3.46	0.32		0.32
153	Brindley (1951)	21.40	0.89	25.40	0.25	37.60	2.04	0.05	0.13		87.98	2.42	0.08	1.58	1.80	0.02	3.55	0.34	0.00	0.12
154	Brindley (1951)											2.48	0.30	1.22	1.82	0.04	3.46	0.32		0.32
155	Bannister & Whittard (1945)	26.40		18.23	5.70	25.87	11.35	0.04	0.76		88.35	2.83		1.17	1.13	0.46	2.32	1.81	0.00	0.18
156	Hutton & Seelye (1945)	27.64	0.22	22.48	0.06	12.06	24.32	0.02	0.23	0.06	87.09	2.73	0.02	1.27	1.34	0.00	0.99	3.57	0.00	0.01
157	Hutton & Seelye (1945)	31.87	0.17	14.51	1.86	3.57	32.76		0.06	1.38	86.18	3.07	0.01	0.93	0.72	0.14	0.29	4.71		0
158	Engelhardt (1942)	20.82		17.64	8.70	37.96	4.15				89.27	2.42		1.58	0.83	0.76	3.69	0.72		0.00
159	Engelhardt (1942)	26.65		16.14	6.69	34.43	4.47				88.38	2.99		1.01	1.12	0.56	3.23	0.75		0.34
160	Hödl (1942)	22.47		23.57	4.01	29.27	9.81				89.13	2.42		1.58	1.40	0.32	2.63	1.57		0.07
161	Hutton (1940)	26.45		20.88	2.82	21.06	16.84	0.44	0.47		88.96	2.71		1.29	1.24	0.22	1.81	2.57	0.04	0.06
162	Lazarenko (1940)											3.09		0.91	3.92	0.05		0.21		1.44
163	Lazarenko (1940)											3.06		0.94	3.88	0.08		0.23		1.40
164	Lazarenko (1940)											3.10		0.90	4.16	0.07		0.11		1.67
165	Hallimond *et al.* (1939)											2.80		1.20	0.86	0.60	3.56	0.78	0.04	0.13
166	Hallimond *et al.* (1939)	24.35	0.04	20.21	2.13	36.27	5.57	0.48	0.10		89.15	2.70	0.00	1.30	1.35	0.18	3.37	0.92	0.05	0.12
167	Hallimond *et al.* (1939)	24.90		15.60	7.20	35.00	4.60	0.40			87.70	2.86		1.14	0.97	0.62	3.36	0.79	0.04	0.22
168	Nockolds & Richey (1939)	25.07	0.12	19.78	3.50	35.80	1.11	0.50	2.15		88.03	2.85	0.01	1.15	1.50	0.30	3.40	0.19	0.05	0.24
169	Holzner (1937)	25.09	0.05	18.94	9.60	25.66	9.80	0.02	0.49		89.65	2.68	0.00	1.32	1.06	0.77	2.29	1.56	0.00	0.24
170	Holzner (1937)	22.18	0.04	20.04	7.35	35.23	3.79	0.02	0.49		90.60	2.51	0.00	1.49	1.18	0.63	3.33	0.64	0.00	0.15
171	Hutton (1938)	26.69	0.30	19.57	3.49	21.80	16.23	0.30	0.17	0.13	88.68	2.76	0.02	1.24	1.15	0.27	1.89	2.50	0.03	0.09
172	Mélon (1938)	27.56		24.47	3.85	10.51	20.86	1.80			89.05	2.68		1.32	1.48	0.28	0.85	3.02	0.15	0.22
173	Tilley (1938)	25.62	0.88	21.19	3.88	21.55	15.28	0.35	0.16		88.91	2.64	0.07	1.36	1.22	0.30	1.86	2.35	0.03	0.08
174	Simpson (1937)	23.32	0.03	17.45	4.09	38.90	4.54	0.01	0.24		88.58	2.68	0.00	1.32	1.05	0.35	3.74	0.78	0.00	0.04
175	Simpson (1936)	23.43		18.21	4.49	36.30	5.41				87.84	2.68		1.32	1.13	0.39	3.47	0.92		0.10
176	Ross (1935)	24.60		19.10	3.12	29.04	13.10				88.96	2.64		1.36	1.06	0.25	2.61	2.10		0

(continued)

TABLE 2. (*contd.*)

N°	Reference	Method	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	MnO	$CaO + Na_2O + K_2O$	Others	Total	Si	Ti	^{IV}Al	^{VI}Al	Fe^{3+}	Fe^{2+}	Mg	Mn	□
177	Jung (1931)		26.65		16.14	6.69	34.43	4.47				88.38	2.99		1.01	1.12	0.56	3.23	0.75		0.34
178	Dschang (1931)		30.30		18.25	2.64	3.98	32.66		0.03		88.24	2.87		1.13	0.90	0.19	0.32	4.61		0
179	Jung & Kohler (1930)		20.82		17.64	8.70	37.96	4.15				89.27	2.42		1.58	0.83	0.76	3.69	0.72		0.00
180	Orcel, 1927, p246		22.27	0.08	21.40	0.67	43.01	2.35	0.05	0.15		90.33	2.54	0.01	1.46	1.41	0.06	4.10	0.40	0.00	0.00
181	Orcel (1927)		26.50	0.03	20.85	1.90	18.73	19.85	0.52			88.38	2.69	0.00	1.31	1.19	0.15	1.59	3.01	0.04	0.01
182	Orcel (1927)		25.35		22.06	18.97	8.36	15.06	0.08			89.88	2.52		1.48	1.11	1.42	0.70	2.24	0.01	0.53
183	Orcel (1927)		27.12		27.68	0.20	1.24	30.96	0.54			87.74	2.51		1.49	1.54	0.01	0.10	4.28	0.04	0.03
184	Chernykh (1926)		25.04		20.10	2.05	35.40	4.28				86.87	2.83		1.17	1.51	0.17	3.34	0.72		0.25
185	Shannon & Wherry (1922)		23.20		24.42	3.48	13.40	32.76		1.04		88.30	2.10		1.90	0.71	0.24	1.01	4.42		0
186	Shannon & Wherry (1922)		27.78		24.30	1.43	0.35	32.71				86.57	2.61		1.39	1.29	0.10	0.03	4.58		0.00
187	Poitevin & Graham (1918)		24.40		22.77	0.45		32.70	0.09	0.40		80.81	2.47		1.53	1.18	0.03		4.93	0.01	0
188	Dana (1915)		33.24		11.07	2.26	25.11	16.51	0.41	1.36		89.96	3.42		0.58	0.77	0.18	2.16	2.53	0.04	0.16
189	Tschermak (1891)		23.62		22.26		38.97	1.09	0.98	1.67		88.59	2.68		1.32	1.67		3.70	0.18	0.09	0.03
190	Tschermak (1891)		33.83		12.95	2.25	3.02	34.94				86.99	3.21		0.79	0.65	0.16	0.24	4.94		0.01
191	Hawes (1875)		33.46		10.96	2.56	24.72	16.52	0.40	1.21		89.83	3.44		0.56	0.77	0.20	2.13	2.53	0.03	0.18

Footnote: Speciation of Fe was obtained using chemical titration (CHE) or, for the past 20 years, using XANES (XAN), Mössbauer (MÖS) or XPS spectroscopies. Where no method is indicated, chemical titration is assumed.

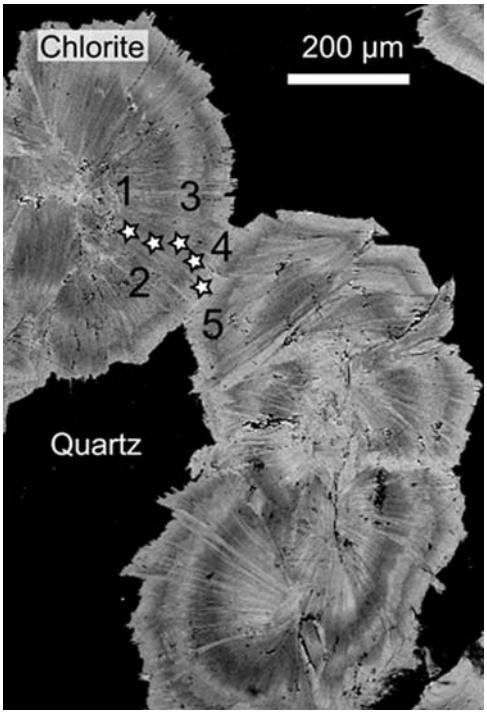

FIG. 1. Backscattered-electron image of an oscillatory-zoned chlorite showing Al-free di-trioctahedral substitution, from the Pic-de-Port-Vieux, Pyrenees, Spain. The numbers refer to the structural formulae reported in Table 2.

rather than by changes in the buffering assemblage (Lanari *et al.* 2014a; Trincal *et al.*, 2015). Most of the spot analyses reported in the literature correspond to different geological environments (Table 2); it is thus very difficult to use them to evaluate the link between the Fe^{3+} behaviour and the evolution of a parameter such as pressure, temperature, f_{O_2}, *etc*.

The choice of analytical method to estimate the XFe^{3+} in chlorite is essential. Chlorite Fe^{3+} measurements by Mössbauer spectroscopy or titration are relatively common but provide few constraints due to poor spatial resolution. Indeed, recent investigations using high-resolution mapping (*e.g.* de Andrade *et al.*, 2006; Muñoz *et al.*, 2006) have demonstrated that chlorite is frequently zoned, recording strong compositional variability even at the crystal scale (*e.g.* Lanari *et al.*, 2014b). Compositional zoning reflects time series of equilibrium conditions experienced by the rock. Thus *in situ* micrometric analyses are required to ensure a precise determination of the Fe^{3+}/Fe_{Tot} of the successive growth zones, which is impossible using Mössbauer spectroscopy. µ-XANES XFe^{3+} spot analyses or mapping allow us to elucidate the heterogeneity of the Fe chemistry of chlorite which is critical to see the relations between formation temperature and crystal geometry (Vidal *et al.*, 2006; Trincal *et al.*, 2015).

µXANES DATA FROM ZONED CHLORITES

Accurate *in situ* µXANES and electron microprobe analyses performed on zoned chlorite from the Sambagawa metamorphic belt in Japan (Vidal *et al.*, 2006) and on oscillatory-zoned chlorite from hydrothermal veins in the Pic-de-Port-Vieux, Pyrenees, Spain (fig. 1 from Trincal *et al.*, 2015) show variations in the composition of the Fe^{3+}, Mg and Fe^{2+} cation proportions, while that of Si and Al remain constant (Table 2, Fig. 2). This trend is observed independently in both samples, which have different bulk-rock compositions and experienced different metamorphic conditions. Indeed, chlorite from Japan comes from a blueschist-facies metapelite made of K-white mica, garnet, albite, quartz and graphite (Vidal *et al.*, 2006), while the chlorite from the Pyrenees crystallizes in a vein of a greenschist-facies metapelite without garnet or graphite (Trincal *et al.*, 2015). The absence of graphite is a good indicator of more oxidizing conditions. In both cases, XFe^{3+} increases as temperature decreases, as suggested by numerous authors (*e.g.* Lanari *et al.*, 2014a; Vidal *et al.*, 2016). Furthermore, in both cases, there is no significant change in the Al content of the zoned chlorite. This result excludes the hypothesis of DT, TK or Al-Fe^{3+} substitutions being at the origin of the XFe^{3+} variations.

AL-FREE DI-TRIOCTAHEDRAL SUBSTITUTION

Based on µXANES analyses performed on zoned chlorite by Vidal *et al.* (2006) and Trincal *et al.* (2015), and in agreement with the literature data (Table 2), we demonstrate that a di-trioctahedral substitution implying Fe^{3+} can be used to explain the variations of XFe^{3+} in natural chlorite:

$$2Fe^{3+} + \square = 3(Mg^{2+}, Fe^{2+}) \quad (1)$$

As this substitution does not explicitly involve any Al cations, it is named Al-free di-trioctahedral substitution (AFDT); it must not be confused with the Al-free chlorite end-member.

This substitution is similar to another couple suggested by Billault *et al.* (2002) and based on electron microprobe

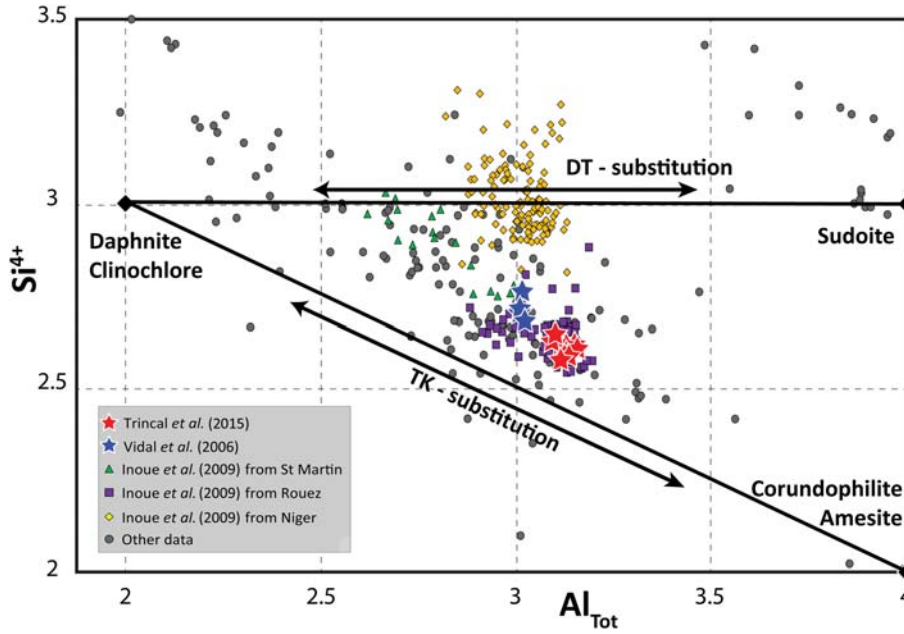

FIG. 2. Compilation of the Fe^{3+}-bearing chlorite compositions. The Si-Al plot is used to highlight the di-trioctahedral (DT) and Tschermak (TK) substitutions. End-members and structural formulae are reported in Tables 1 and 2.

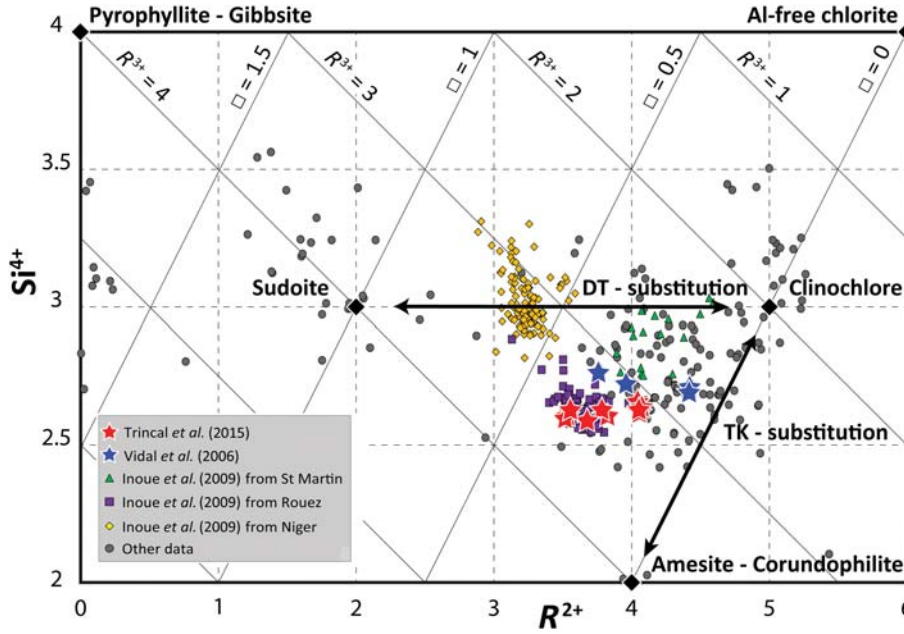

FIG. 3. Compilation of Fe^{3+}-bearing chlorite compositions. The Si^{4+}–R^{2+} plot by Wiewióra & Weiss (1990) is used to highlight the di-trioctahedral (DT) and the Al-Fe^{3+} substitutions.

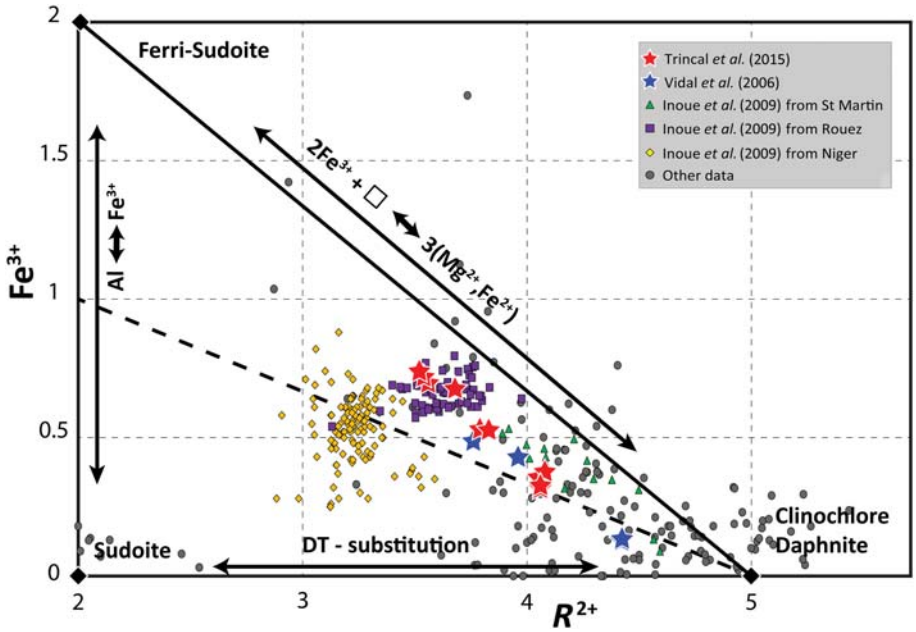

FIG. 4. Compilation of the Fe^{3+}-bearing chlorite compositions. The Fe^{3+}–R^{2+} plot highlights the di-trioctahedral (DT), Al-Fe^{3+} and AFDT substitutions.

and Mössbauer spectroscopic analyses on sudoite:

$$Fe^{3+} = Al_{(VI)} \text{ and } Fe^{2+} + Fe^{3+} + \square = 3(Mg^{2+}) \quad (2)$$

However, chlorite analyses from their study display both Al and *X*Mg variations, which is not the case for the samples in the present study.

Chlorite compositions from Vidal *et al.* (2006) and Trincal *et al.* (2015) are plotted in an Fe^{3+} *vs.* R^{2+} diagram (Fig. 4). In this diagram, data from zoned chlorite are distributed along a line parallel to the AFDT substitution vector. The AFDT substitution allows us to define a theoretical Fe^{3+}-bearing chlorite end-member; namely ferri-sudoite ($(Si_3Al)[(Fe^{2+}, Mg)_2Fe_2^{3+}\square Al)O_{10}(OH)_8$) with two atoms of Fe^{3+} (Table 1). Ferri-sudoite can be separated into ferri-sudoite-Fe ($(Si_3Al)[Fe_2^{2+}Fe_2^{3+}\square Al)O_{10}(OH)_8$) and ferri-sudoite-Mg ($(Si_3Al)[Mg_2Fe_2^{3+}\square Al)O_{10}(OH)_8$). As Fe^{3+} replaces Mg and Fe^{2+}, it seems convenient to allocate up two atoms of Fe^{3+} to the M2-M3 sites (total multiplicity of 4) leaving Al in the M4 (Table 1).

According to several authors, the Fe^{3+} cation seems limited to 1 a.p.f.u and is generally allocated to the M4 site following the Al-Fe^{3+} substitution. This last assertion is supported by Z-contrast images of high-angle annular dark-field imaging-scanning transmission electron microscopy (HAADF-STEM) and other studies (*e.g.* Smyth *et al.*, 1997; Inoue & Kogure, 2016; Vidal *et al.*, 2016). Among data collected in the literature, only six analyses show Fe^{3+} contents of >1 a.p.f.u (Orcel, 1927; Brindley & Youell, 1953; Malysheva *et al.*, 1977; Goodman & Bain, 1979; Kodama *et al.*, 1982; Singer *et al.*, 2009 in Table 2). However, these analyses would actually match other phyllosilicates, suggesting contamination issues. Although AFDT substitution suggests that it is possible, no sudoite with >1 Fe^{3+} atom has been yet discovered; it offers interesting research opportunities.

CONCLUSION

The compilation of Fe^{3+}-bearing chlorite analyses in this study, especially those acquired by µXANES spectroscopy in zoned crystals, suggests the existence of a new chlorite substitution, the AFDT substitution that is characterized by $2Fe^{3+} + \square = 3(Mg^{2+}, Fe^{2+})$ and implies a new chlorite end-member: ferri-sudoite $(Si_3Al)[(Fe^{2+},Mg)_2Fe_2^{3+}\square Al)O_{10}(OH)_8$ with 2 atoms of Fe^{3+}. These results are not in agreement with previous studies which showed Al-Fe^{3+} substitution implying only 1 Fe^{3+}. The absence of constraints on the Fe^{3+} crystallographic position together with the Fe^{3+} ionic properties in chlorite require further studies to confirm

the existence of the AFDT substitution and of the ferri-sudoite end-member, *e.g.* with accurate *in situ* Fe^{3+} measurements in synthetic or diagenetic chlorite formed in different oxidizing environments. This study opens the door for further research developments that would have strong implications, *e.g.* in chlorite geothermometry.

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