

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

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(Received: 1 November 2015; revised: 30 April 2016; Guest editor: Atsuyuki Inoue)

DOI: 10.1180/claymin.2016.051.4.09

Abstract

A compilation of Fe³⁺-bearing chlorite analyses is used 1) to investigate the Al-free di-trioctahedral (AFDT) substitution $2\text{Fe}^{3+} + \square = 3(\text{Mg}, \text{Fe}^{2+})$ in chlorite and 2) to estimate the composition of a ferri-sudoite end-member $(\text{Si}_3\text{Al}) [(\text{Fe}^{2+}, \text{Mg})_2 \text{Fe}^{3+}_2 \square \text{Al}] \text{O}_{10}(\text{OH})_8$ within the chlorite solid-solution domain. According to our observations, up to two Fe³⁺ 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+} ($\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$) in heterogeneous chlorite. Although, further studies are required to confirm the crystallographic position of Fe³⁺ and refine its ionic/magnetic behaviour in chlorite, it opens perspectives for developing new geothermometers.

Introduction



Chlorite is an 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: $\text{R}^{2+}_{6-x-3y}\text{R}^{3+}_{x+2y}\square_y(\text{Si}_{4-x}\text{R}^{3+}_x)\text{O}_{10}(\text{OH})_8$, in which R^{2+} represents divalent cations, R^{3+} trivalent cations and \square octahedral vacancies (e.g., Wiewiora and 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 ones (denoted M1, M2). Two other octahedral sites (M3 and M4) are located in the brucite interlayer. Al^{VI} or trivalent Fe^{3+} cations are preferentially located 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 closed 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) $\text{Si}^{4+}_{(\text{IV})} + (\text{Fe}^{2+}, \text{Mg}^{2+})_{(\text{VI})} = \text{Al}^{3+}_{(\text{IV})} + \text{Al}^{3+}_{(\text{VI})}$; ferromagnesian (FM) $\text{Mg}^{2+}_{(\text{VI})} = \text{Fe}^{2+}_{(\text{VI})}$ and di-trioctahedral (DT) $2\text{Al}^{3+}_{(\text{VI})} + \square_{(\text{VI})} = 3(\text{Mg}^{2+}, \text{Fe}^{2+})_{(\text{VI})}$. Two filling models are used in the literature for the distribution of cations on the crystallographic sites. The first model called "disorderly", considers that there is no preferred configuration (e.g., Inoue et al., 2009). The second model called "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} in M4 then M1 and then eventually in M2-M3, Fe and Mg in M2-M3 then in M1. Following the equipartition assumption, $X_{\text{Mg}} (\text{Mg}^{2+}/(\text{Mg}^{2+}+\text{Fe}^{2+}))$ is considered to be equal between M1 and M2-M3 sites. Several chlorite end-members are classically defined (Table 1): Al-free chlorite (Si_4) $[\text{Mg}_6]\text{O}_{10}(\text{OH})$, amesite (Si_2Al_2) $[(\text{Fe}^{2+}, \text{Mg})_4\text{Al}_2]\text{O}_{10}(\text{OH})_8$, clinocllore (Si_3Al) $[\text{Mg}_5\text{Al}]$

$\text{O}_{10}(\text{OH})_8$, corundophilite $(\text{Si}_2\text{Al}_2) [\text{Mg}_4\text{Al}_2] \text{O}_{10}(\text{OH})_8$, daphnite $(\text{Si}_3\text{Al}) [\text{Fe}^{2+}_5 \text{Al}] \text{O}_{10}(\text{OH})_8$, pyrophyllite-gibbsite $(\text{Si}_4) [\text{Al}_4\Box_2] \text{O}_{10}(\text{OH})_8$ and sudoite $(\text{Si}_3\text{Al}) [(\text{Fe}^{2+}, \text{Mg})_2 \Box \text{Al}_3] \text{O}_{10}(\text{OH})_8$. These end-members do not include any ferric iron component.

For fifteen years, several authors have emphasised the importance of Fe^{3+} in chlorite, particularly for their 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 (Tchermak, 1891; Orcel, 1927; Hallimond et al., 1939; Brindley, 1951), Mössbauer (Pal et al., 1993; Aja and Dyar, 2000; Inoue et al., 2009), XPS (Inoue et al., 2010) and μ -XANES spectroscopies (Wilke et al., 2001; Vidal et al., 2006; Rigault, 2010; Trincal et al., 2015).

Chlorite data from literature

A compilation of almost two hundred 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; other one experienced diagenetic to metamorphic conditions as oscillatory zoning chlorites from the Pic-de-Port-Vieux outcrop (Figure 1; Trincal et al., 2015). In addition, 202 data from three localities were incorporated in this review (Inoue et al., 2009). Most of the selected chlorite contain (in a.p.f.u, see [Table 2](#)): 2.5 to 3.5 Si^{4+} , 2 to 4

Al^{3+} (Figure 2), 1.5 to 5.5 R^{2+} (Mg^{2+} , Mn^{2+} , Fe^{2+}) (Figure 3) and less than 1 Fe^{3+} (Figure 4). These analyses are distributed between classical end-members and apparently follow the classical DT and TK substitutions (Figures 2, 3) or the Al-Fe^{3+} substitution (Figure 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 the data from Inoue et al. (2009), which show relationships between sampling localities and chlorite structural formulae and oxidation state (Figures 2, 3 and 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, 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 the 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 little constraints due to poor spatial resolution. Indeed, recent investigations using high-resolution mapping (e.g., deAndrade et al., 2006; Muñoz et al., 2006), 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 $\text{Fe}^{3+}/\text{Fe}_{\text{Tot}}$ of the successive growth zones, which is impossible using Mössbauer spectroscopy. μ -XANES XFe^{3+} spot analyses or mapping allow highlighting iron chemistry heterogeneity of

chlorite, which is critical to see the relations between formation temperature and crystal geometry (Vidal et al., 2006; Trincal et al., 2015).

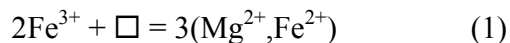
μXANES data from zoned chlorites

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 zoning chlorite from hydrothermal veins in the Pic-de-Port-Vieux, Pyrenees, Spain (Figure 1; 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, Figure 2). This trend is independently observed 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 chlorite from 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, from 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

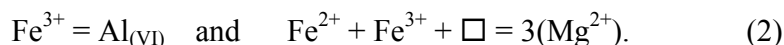
Based on μXANES analyses performed on zoned chlorite by Vidal et al. (2006) and Trincal et al. (2015), and in agreement with the literature data (Table 2), we demonstrate that a

di/trioctahedral substitution implying Fe^{3+} can be used to explain the variations of XFe^{3+} in natural chlorite:



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 Al-free chlorite end-member.

This substitution is similar to another couple suggested by Billaut et al. (2002) and based on electron microprobe and Mössbauer spectroscopic analyses on sudoite:



However, chlorite analyses from their study display both Al and X_{Mg} variations, which is not our case.

Chlorite compositions from Vidal et al. (2006) and Trincal et al. (2015) are plotted in a Fe^{3+} versus R^{2+} diagram (Figure 4). In this diagram, data from zoned chlorite are distributed along a line parallel to AFDT substitution vector. The AFDT substitution allows to define a theoretical Fe^{3+} -bearing chlorite end-member; namely ferri-sudoite $((\text{Si}_3\text{Al}) [(\text{Fe}^{2+}, \text{Mg})_2 \text{Fe}^{3+}_2 \square \text{Al}] \text{O}_{10}(\text{OH})_8)$ with two atoms of Fe^{3+} (Table 1). Ferri-sudoite can be separated into ferri-sudoite-Fe $((\text{Si}_3\text{Al}) [\text{Fe}^{2+}_2 \text{Fe}^{3+}_2 \square \text{Al}] \text{O}_{10}(\text{OH})_8)$ and ferri-sudoite-Mg $((\text{Si}_3\text{Al}) [\text{Mg}_2 \text{Fe}^{3+}_2 \square \text{Al}] \text{O}_{10}(\text{OH})_8)$. 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 2) leaving Al in the M4 (Table 1).

According to several authors, 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 HAADF-STEM and others studies (e.g. Smyth et al., 1997; Inoue & Kogure, 2016; Vidal *et al.*, 2016). Among data collected in the literature, only 6 analyses show Fe^{3+} content higher to 1 a.p.f.u (Orcel, 1927; Brindley and Youell, 1953; Malysheva et al., 1977;

Goodman et al., 1979; Kodama et al., 1982; Singer et al., 2009 in Table 2). However, these analyses would actually match to other phyllosilicates, suggesting contamination issues. Although AFDT substitution suggests that it is possible, no sudoite with more than one Fe^{3+} atom has been yet discovered; it opens interesting research opportunities.

Conclusion

The compilation of Fe^{3+} -bearing chlorite analyses made 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 $2\text{Fe}^{3+} + \square = 3(\text{Mg}^{2+}, \text{Fe}^{2+})$ and implies a new chlorite end-member: the ferri-sudoite $(\text{Si}_3\text{Al})[(\text{Fe}^{2+}, \text{Mg})_2\text{Fe}^{3+}_2\square\text{Al}]\text{O}_{10}(\text{OH})_8$ with two atoms of Fe^{3+} . These results are not in agreement with previous studies that showed Al- Fe^{3+} substitution implying only one 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, for example with accurate in-situ Fe^{3+} measurements in synthetic or diagenetic chlorite formed in different oxidizing environments. This study opens the door to further research developments that would have strong implications, for example in chlorite geothermometry.

Acknowledgement

Authors wish to thank Daniel Beaufort, Olivier Vidal and Martin Engi for fruitful discussions regarding Fe^{3+} in chlorite; Atsuyuki Inoue, Fernando Nieto-Garcia and another referee for the valuable advice made to the manuscript; and Flavien Choulet for language corrections.

Figures and Tables

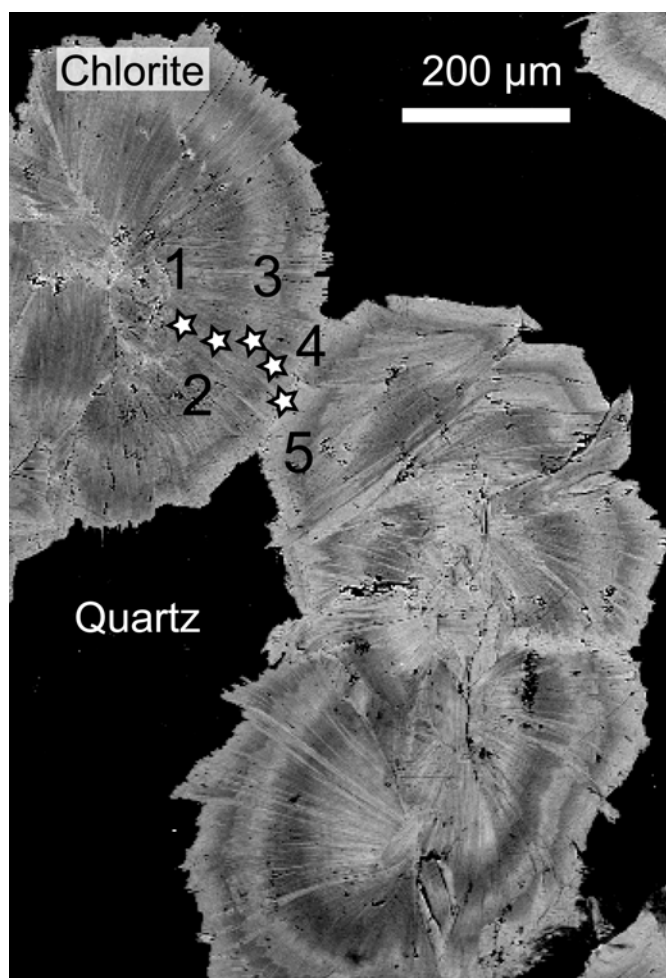


Figure 1 : Backscattered-electron image of an oscillatory zoning chlorite showing Al-Free Di-Trioctahedral substitution, from the Pic-de-Port-Vieux, Pyrenees, Spain. Numbers refer to structural formula reported in Table 2.

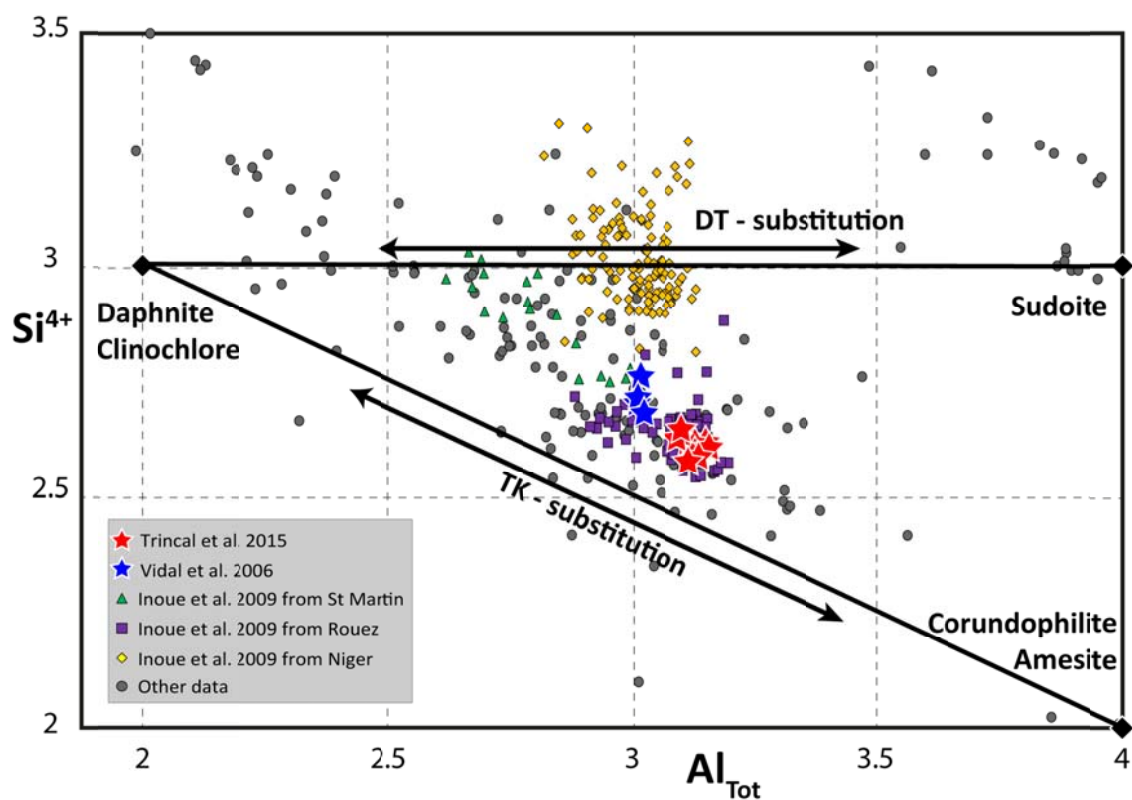


Figure 2: Compilation of the Fe^{3+} -bearing chlorite compositions. The Si - Al plot is used to highlight the di-trioctahedral (DT) and Tschermak (TK) substitutions. End-members and structural formulas are reported in tables 1 and 2.

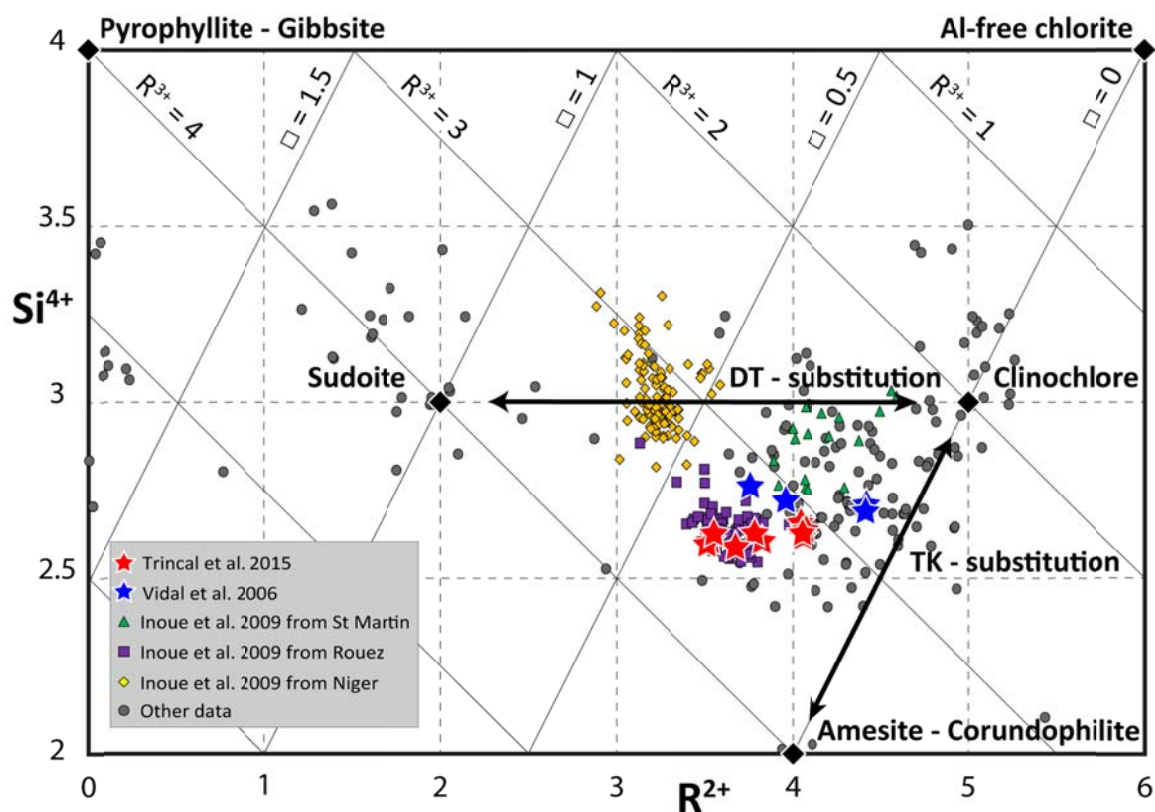


Figure 3: Compilation of Fe^{3+} -bearing chlorite compositions. The Si^{4+} - R^{2+} plot by Wiewiora and Weiss (1990) is used to highlight the di-trioctahedral (DT), Al- Fe^{3+} and new AFDT substitutions.

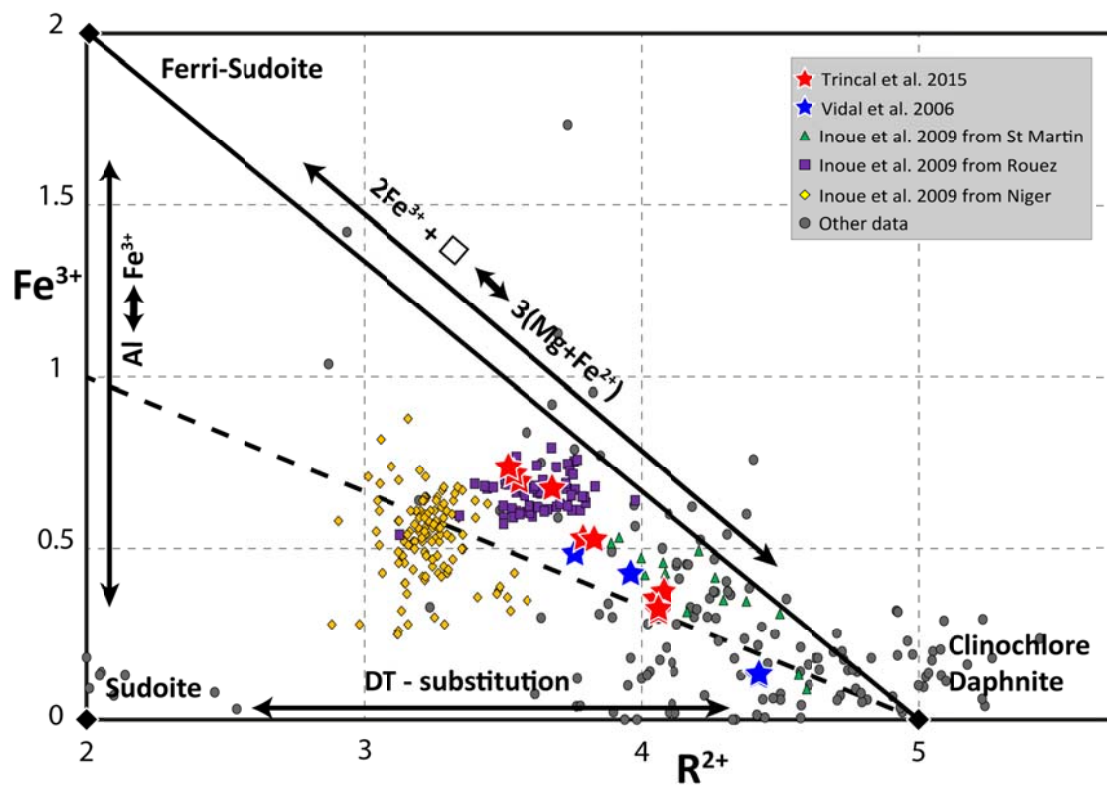


Figure 4: Compilation of the Fe^{3+} -bearing chlorite compositions. The Fe^{3+} - R^{2+} plot highlights the di-trioctahedral (DT), Al- Fe^{3+} and new AFDT substitutions.

Table 1 : Classical chlorite end-members and new ferri-sudoite end-member structural formula. The numbers in brackets refer to the quantity of atoms by structural formula distributed in tetrahedral (T) or octahedral (M) sites.

	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

Table 2: Fe³⁺-bearing chlorites structural formula compilation, calculated on the basis of O = 14. Speciation of iron was obtained using chemical titration (CHE) or, since twenty years, using XANES (XAN), Mössbauer (MÖS) or XPS spectroscopies.

Cf. attached xls file

References

- Ahn, J.H., and Buseck, P.R. (1988) Al-chlorite as a hydration reaction product of andalusite. *Mineralogical Magazine*, 52, 396–399.
- Aja, S.U., and Dyar, D.M. (2002) The stability of Fe–Mg chlorites in hydrothermal solutions—I. Results of experimental investigations. *Applied Geochemistry*, 17, 1219–1239.
- Aleksandrova, V.A., Drits, V.A., and Sokolova, G.V. (1972) Structural features of dioctahedral one-packet chlorite. *Soviet Physics–Crystallography*, 17, 456–461.
- Alysheva, E.I., Rusinova, O.V., and Chekvaidze, V.B. (1977) On sudoites from the polymetal deposits of Rydnyy Altai. *Doklady Akademii Nauk SSSR*, 236, 722–724.
- Anceau, A. (1992) Sudoite in some Visean (lower Carboniferous) K-bentonites from Belgium. *Clay Minerals*, 27, 283–292.
- Ballet, O., Coey, J.M.D., and Burke, K.J. (1985) Magnetic properties of sheet silicates; 2: 1: 1 layer minerals. *Physics and Chemistry of Minerals*, 12, 370–378.
- Bailey, S.W. (1988) *Hydrous phyllosilicates*. American Mineralogical Society, Washington, DC.
- Bannister, F.A., and Whittard, W.F. (1945) A Magnesian Chamosite from the Wenlock Limestone of Wickwar, Gloucestershire. *Mineralogical Magazine*, 27, 99–111.
- Banno, S. (1964) Petrologic studies on Sanbagawa crystalline schists in the Bessi-Ino district, central Sikoku, Japan. *J. Fac. Sci., Univ. Tokyo, Sec. II*, 15, 203–319.
- Bathey, M.H. (1956) The petrogenesis of a spilitic rock series from New Zealand. *Geological magazine*, 93, 89–110.
- Bertoldi, C., Benisek, A., Cemic, L., and Dachs, E. (2001) The heat capacity of two natural chlorite group minerals derived from differential scanning calorimetry. *Physics and Chemistry of Minerals*, 28, 332–336.
- Bilgrami, S.A., and Howie, R.A. (1960) The mineralogy and petrology of a rodingite dike, Hindubagh, Pakistan. *American Mineralogist*, 45, 791–801.
- Billault, V., Beaufort, D., Patrier, P., and Petit, S. (2002) Crystal chemistry of Fe-sudoites from uranium deposits in the Athabasca basin (Saskatchewan, Canada). *Clays and Clay Minerals*, 50, 70–81.
- Borggaard, O.K., Lindgreen, H.B., and Morup, S. (1982) Oxidation and reduction of structural iron in chlorite at 480°C. *Clays Clay Miner*, 30, 353–364.
- Bourdelle, F., Benzerara, K., Beyssac, O., Cosmidis, J., Neuville, D.R., Jr, G.E.B., and Paineau, E. (2013) Quantification of the ferric/ferrous iron ratio in silicates by scanning transmission X-ray microscopy at the Fe L_{2,3} edges. *Contributions to Mineralogy and Petrology*, 166, 423–434.

- Brandt, F., Bosbach, D., Krawczyk-Bärsch, E., Arnold, T., and Bernhard, G. (2003) Chlorite dissolution in the acid pH-range: a combined microscopic and macroscopic approach. *Geochimica et Cosmochimica Acta*, 67, 1451–1461.
- Brindley, G.W. (1951) The crystal structure of some chamosite minerals. *Mineral. Mag*, 29.
- Brindley, G.W., and Youell, R.F. (1953) Ferrous Chamosite and Ferric Chamosite. *Mineralogical Magazine*, 30, 57–70.
- Brydon, J.E., Clark, J.S., and Osborne, V. (1961) Dioctahedral chlorite. *The Canadian Mineralogist*, 6, 595–609.
- Caillière, S., Hénin, S., and Pobegu, T. (1962) Présence d'un nouveau type de chlorite dans les "bauxites" de Saint-Paul-de-Fenouillet (Pyrénées orientales). *Compte rendu de l'adadémie des sciences*, 254, 1657–1658.
- Chamberlain, S.C., Robinson, G.W., and Richards, R.P. (1989) Mineralogy of the Alpine veins near Sherbrooke, Quebec. *Mineralogical Record*, 20, 209–20.
- Chernykh, V.V. (1926) Physicochemische Untersuchung der Serpentine und Chlorite. *Mém. Soc. Russe Min. ser2*, 55, 183–194.
- Dana, E.S. (1915) *Descriptive mineralogy*, 659 p. John Wiley & Sons, New York.
- De Andrade, V., Vidal, O., Lewin, E., O'Brien, P., and Agard, P. (2006) Quantification of electron microprobe compositional maps of rock thin sections: an optimized method and examples RID C-2856-2009. *Journal of Metamorphic Geology*, 24, 655–668.
- Debret, B., Bolfan-Casanova, N., Padrón-Navarta, J.A., Martin-Hernandez, F., Andreani, M., Garrido, C.J., Sánchez-Vizcaíno, V.L., Gómez-Pugnaire, M.T., Muñoz, M., and Trcera, N. (2015) Redox state of iron during high-pressure serpentinite dehydration. *Contributions to Mineralogy and Petrology*, 169, 1–18.
- De Grave, E., Vandenbruwaene, J., and Bockstael, M.V. (1987) ⁵⁷Fe Mössbauer spectroscopic analysis of chlorite. *Physics and Chemistry of Minerals*, 15, 173–180.
- De Waal, S.A. (1970) Nickel minerals from Barberton, South Africa: III. Willemseite, a nickel-rich talc. *American Mineralogist*, 55, 31–42.
- Drits, V.A., and Lazarenko, E.K. (1967) Structural and mineralogical characteristics of donbassites. *Mineral Sb Lvov*, 21, 40–48.
- Dschang, G. (1931) *Die Beziehungen zwischen chemischer Zusammensetzung und den physikalisch-optischen Eigenschaften in der Chloritgruppe*. Fischer.
- Engelhardt, W. v (1942) Die Strukturen von Thuringit, Bavalit und Chamosit und ihre Stellung in der Chloritgruppe. *Zeitschrift für Kristallographie-Crystalline Materials*, 104, 142–159.
- Ericsson, M.T., Wäppling, D.R., and Punakivi, M.K. (1977) Mössbauer spectroscopy applied to clay and related minerals. *Geologiska Föreningen i Stockholm Förhandlingar*, 99, 229–244.

- Fransolet, A.M., and Bourguignon, A. (1978) Di/trioctahedral chlorite in quartz veins from the Ardennes, Belgium. *Canadian Mineralogist*, 16, 365–373.
- Frenzel, G., and Schembra, F.W. (1965) Ein dioktaedrischer chlorit vom Kaiserbachthal (Südpfalz). *Neues Jahrb. Mineral., Monatsh.*, 1965, 108–114.
- Fron del, C. (1955) Two chlorites: gonyerite and melanolite. *American Mineralogist*, 40, 1090–1094.
- Ginzburg, A.I. (1953) On lithium chlorite-cookeite. In *Dokl. Akad. Nauk SSSR* Vol. 90, p. 871.
- Gomes, C.S.F. (1967) Alteration of spodumene and lepidolite with formation of dioctahedral chlorite plus dioctahedral chlorite-dioctahedral montmorillonite interstratifications. *Publ. Museu Lab. Mineral. Geol. Univ. Coimbra, Memorias Noticias*, 64, 32–57.
- Goodman, B.A., and Bain, D.C. (1979) Mössbauer Spectra of Chlorites and Their Decomposition Products. In M.M.M. and V.C. Farmer, Ed., *Developments in Sedimentology* Vol. 27, pp. 65–74. Elsevier.
- Gregori, D.A., and Mercader, R.C. (1994) Mössbauer study of some Argentinian chlorites. *Hyperfine Interactions*, 83, 495–498.
- Hallimond, A.F., Harvey, C.O., and Bannister, F.A. (1939) On the Relation of Chamosite and Daphnite to the Chlorite Group. *Mineralogical Magazine*, 25, 441–465.
- Hawes, G.W. (1875) On diabantite, a chlorite occurring in the trap of the Connecticut valley. *American Journal of Science*, 454–457.
- Hayashi, H., and Oinuma, K. (1965) Relationship between infrared absorption spectra in the region of 450-900 CM⁻¹ and chemical composition of chlorite. *American Mineralogist*, 50, 476.
- Hödl, A. (1942) Über Chlorite der Ostalpen. Ein Beitrag zur Systematik der Chlorite. *N. Jb. f. Min., Beil., Bd.*, 77, 1–77.
- Holland, T., Baker, J., and Powell, R. (1998) Mixing properties and activity-composition and relationships of chlorites in the system MgO-FeO-Al₂O₃-SiO₂-H₂O. *European Journal of Mineralogy*, 10, 395–406.
- Holzner, J. (1938) Beiträge zur Kenntnis der varistischen Gesteins-und Mineralprovinz im Lahn-Dillgebiet. *Neues, Jahrb. Min., Bl. Bd.*, 389.
- Honda, S. (1975) Dioctahedral chlorite, closely associated with kaolinite from the Kamikita mine (Kuroko deposit). *Rep. Res. Inst. Underground Res. Mining College Akita Univ.*, 43, 1–8.
- Horikoshi, E. (1965) Kuroko-type exhalative sedimentary mineral deposits. *J. Mining Inst. Kyusyu*, 33, 300–210.
- Hutton, C.O. (1938) *The stilpnomelane group of minerals*. Oxford University Press.
- Hutton, C.O. (1940) *Metamorphism in the lake Wakatipu region, western Otago, New Zealand*, 90 p. E.V. Paul, government printer.

- Hutton, C.O., and Seelye, F.T. (1945) Contributions to the mineralogy of New Zealand-part I. In Transactions of the Royal Society of New Zealand Vol. 75, pp. 160–168. J. Hughes, Printer
- Inoué A. & Kogure T. (2016) High-angle annular dark field scanning transmission electron microscopic (HAADF-STEM) study of Fe-rich 7 Å–14 Å interstratified minerals from a hydrothermal deposit. *Clay Minerals*, in press, DOI: 10.1180/claymin.2016.051.4.05.
- Inoue, A., Meunier, A., Patrier-Mas, P., Rigault, C., Beaufort, D., and Vieillard, P. (2009) Application of chemical geothermometry to low-temperature trioctahedral chlorites. *Clays and Clay Minerals*, 57, 371–382.
- Inoue, A., Kurokawa, K., and Hatta, T. (2010) Application of Chlorite Geothermometry to Hydrothermal Alteration in Toyoha Geothermal System, Southwestern Hokkaido, Japan. *Resource Geology*, 60, 52–70.
- Joswig, W., and Fuess, H. (1990) Refinement of a one-layer triclinic chlorite. *Clays and Clay Minerals*, 38, 216–218.
- Jung, H., and Köhler, E. (1930) Untersuchungen über den Thuringit von Schmiedefeld in Thüringen. *Chemie der Erde*, 5, 182.
- Jung, H. (1931) Untersuchungen über den Chamosit von Schmiedefeld i. Thur. *Chem. Erde*, 6, 275–306.
- Jung, H., and Köhler, E. (1930) Untersuchungen über den Thuringit von Schmiedefeld in Thüringen. *Chemie der Erde*, 5, 182.
- Kawano, M., and Tomita, K. (1991) Mineralogy and genesis of clays in postmagmatic alteration zones, Makurazaki volcanic area, Kagoshima prefecture, Japan. *Clays and Clay Minerals*, 39, 597–608.
- Kimbara, K., and Nagata, H. (1974) Clay minerals in the core samples of the mineralized zone of Niida, southern part of Odate Akita Prefecture, Japan. *Japanese Association of Mineralogists, Petrologists and Economic Geologists Journal*, 69, 239–254.
- Kimbara, K., Shimoda, S., and Sudo, T. (1973) An Unusual Chlorite as Revealed by the High Temperature X-Ray Diffractometer. *Clay Minerals*, 10, 71–78.
- Kimbara, K., and Sudo, T. (1973) Chloritic clay minerals in tuffaceous sandstone of the Miocene Green Tuff formation, Yamanaka district, Ishikawa Prefecture, Japan. *J. Japan. Assoc. Miner. Petrol. Econ. Geol.*, 68, 246–258.
- Kittrick, J.A. (1982) Solubility of two high-Mg and two high-Fe chlorites using multiple equilibria. *Clays and Clay Minerals*, 30, 167–179.
- Kodama, H., Longworth, G., and Townsend, M.G. (1982) A Mössbauer investigation of some chlorites and their oxidation products. *Canadian Mineralogist*, 20, 585–592.
- Kramm, U. (1980) Sudoite in low-grade metamorphic manganese rich assemblages. *Neues Jahrb Mineral Abh*, 138, 1–13.

- Lanari, P., Wagner, T., and Vidal, O. (2014a) A thermodynamic model for di-trioctahedral chlorite from experimental and natural data in the system $\text{MgO-FeO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$: applications to P-T sections and geothermometry. *Contributions to Mineralogy and Petrology*, 167, 1–19.
- Lanari, P., Vidal, O., De Andrade, V., Dubacq, B., Lewin, E., Grosch, E.G., and Schwartz, S. (2014b) XMapTools: A MATLAB©-based program for electron microprobe X-ray image processing and geothermobarometry. *Computers & Geosciences*, 62, 227–240.
- Lapham, D.M. (1958) Structural and chemical variation in chromium chlorite. *American Mineralogist*, 43, 921–956.
- Laird, J. (1988) Chlorites; metamorphic petrology. *Reviews in Mineralogy and Geochemistry*, 19, 405–453.
- Lazarenko, E.K. (1940) Donbassites, a new group of minerals from the Donetz Basin. *CR Acad. Sci. URSS*, 28, 519–521.
- Lin, C.Y., and Bailey, S.W. (1985) Structural data for sudoite. *Clays and Clay Minerals*, 33, 410–414.
- Lougear, A., Grodzicki, M., Bertoldi, C., Trautwein, A.X., Steiner, K., and Amthauer, G. (2000) Mössbauer and molecular orbital study of chlorites. *Physics and Chemistry of Minerals*, 27, 258–269.
- MacKenzie, K.J.D., and Bowden, M.E. (1983) Thermal and Mössbauer studies of iron-containing hydrous silicates. IV. Amesite. *Thermochimica Acta*, 64, 83–106.
- Malmström, M., Banwart, S., Lewenhagen, J., Duro, L., and Bruno, J. (1996) The dissolution of biotite and chlorite at 25°C in the near-neutral pH region. *Journal of Contaminant Hydrology*, 21, 201–213.
- Malysheva, T.V., Satarova, L.M., and Polyakova, N.P. (1977) Thermal transformations of layered silicates and the nature of the iron-bearing phase in the CII type Murray carbonaceous chondrite. *Geokhimiya*, 8, 1136–1148.
- Mathias, M. (1952) A note on two actinolites and a chlorite from the Prieska district, Cape Province: *Trans. and Proc. Geol. Soc. S. Africa*, 55, 13–18.
- May, H.M., Acker, J.G., Smyth, J.R., Bricker, O.P., and Dyar, M.D. (1995) Aqueous dissolution of low-iron chlorite in dilute acid solutions at 25 C. *Clay Minerals Society Proceedings*, Abstract, 32, 88.
- Mélon, J. (1938) Description des chlorites et clintonites belges. *Palais des Académies*.
- Meunier, A. (2005) *Clays*, 490 p. Springer Science & Business Media.
- Mitra, S., and Bidyananda, M. (2001) Crystallo-Chemical Characteristics of Chlorites from the Greenstone Belt of South India, and Their Geothermometric Significance. *Clay Science*, 11, 479–501.

- Muñoz, M., De Andrade, V., Vidal, O., Lewin, E., Pascarelli, S., and Susini, J. (2006) Redox and speciation micromapping using dispersive X-ray absorption spectroscopy: Application to iron chlorite mineral of a metamorphic rock thin section. *Geochemistry Geophysics Geosystems*, 7.
- Nakamura, T. (1960) On chlorite from the Ashio copper mine, Japan. *Mineral. J.*, 4, 383–397.
- Nockholds, S.R., and Richey, J.E. (1939) Replacement veins in the Mourne Mountains granites, N. Ireland. *American Journal of Science*, 237, 27–47.
- Orcel, J. (1927) Recherches sur la composition chimique des chlorites. Société Générale d’Imprimerie et d’édition.
- Pal, T., Maity, P.K., Das, D., and Mitra, S. (1993) Oxidation character of chlorite from Byrapur chromite deposit, India — A57Fe Mössbauer evaluation. *Bulletin of Materials Science*, 16, 229–237.
- Phillips, T.L., Loveless, J.K., and Bailey, S.W. (1980) Cr³⁺ coordination in chlorites: a structural study of ten chromian chlorites. *American Mineralogist*, 65, 112–122.
- Poitevin, E., and Graham, R.P.D. (1918) Contributions to the mineralogy of Black Lake area, Quebec. Government Printing Bureau.
- Post, J.L., and Plummer, C.C. (1972) The chlorite series of Flagstaff Hill area, California: A preliminary investigation. *Clays Clay Miner*, 20, 271–83.
- Rigault, C. (2010) Cristallochimie du fer dans les chlorites de basse température : implications pour la géothermométrie et la détermination des paléoconditions redox dans les gisements d’uranium. Thèse de doctorat, Université de Poitiers.
- Ross, C.S. (1935) Origin of the copper deposits of the Ducktown type in the southern Appalachian region. US Gov’t. Print. Off.
- Rule, A.C., and Bailey, S.W. (1987) Refinement of the crystal structure of a monoclinic ferroan clinocllore. *Clays and Clay Minerals*, 35, 129–138.
- Shannon, E.V., and Wherry (1922) Notes on white chlorites. *Journ. Wash. Acad. Sci.*, 12, 239.
- Shimane, H., and Sudo, T. (1958) A chloritic mineral found associated with vermiculite. *Clay Minerals Bull*, 3, 297–301.
- Shimoda, S. (1970) An Expandable Chlorite-Like Mineral from the Hanaoka Mine, Akita Prefecture, Japan. *Clay Min. Bull*, 8, 352–359.
- Shirozu, H. (1958) X-ray powder patterns and cell dimensions of some chlorites in Japan, with a note on their interference colors. *Mineralogical Journal*, 2, 209–223.
- Simpson, E.S. (1936) Contributions to the mineralogy of Western Australia. *Royal Society of Western Australia Journal*, 22, 1–18.
- Simpson, E.S. (1937) Ditto. *Royal Society of Western Australia Journal*, 23, 17–35.

- Singer, D.M., Maher, K., and Brown Jr., G.E. (2009) Uranyl–chlorite sorption/desorption: Evaluation of different U(VI) sequestration processes. *Geochimica et Cosmochimica Acta*, 73, 5989–6007.
- Smyth, J.R., Dyar, M.D., May, H.M., Bricker, O.P., and Acker, J.G. (1997) Crystal structure refinement and Mössbauer spectroscopy of an ordered, triclinic clinocllore. *Clays and Clay Minerals*, 45, 544–550.
- Spanu, V., Filoti, G., Ionescu, J., and Medesan, A. (1977) Mössbauer study of some chlorites. In *Proceedings of the International Conference on Mössbauer Spectroscopy*, Editorial Group of the *Revue Roumaine de Physique*, Bucharest pp. 323–324.
- Stone, R.L., and Weiss, E.J. (1955) Examination of Four Coarsely Crystalline Chlorites by X-ray and High-Pressure DTA Techniques. *Clay Minerals*, 2, 214–222.
- Sudo, T., and Shimoda, S. (1978) *Clays and clay minerals of Japan* Vol. 26. Elsevier.
- Tilley, C.E. (1938) The status of hornblende in low grade metamorphic zones of green schists. *Geological Magazine*, 75, 497–511.
- Trincal, V., Lanari, P., Buatier, M., Lacroix, B., Charpentier, D., Labaume, P., and Muñoz, M. (2015) Temperature micro-mapping in oscillatory-zoned chlorite: Application to study of a green-schist facies fault zone in the Pyrenean Axial Zone (Spain). *American Mineralogist*, 100, 2468–2483.
- Tschermak, G. (1891) Die chloritgruppe. *Sitzber. Akad. Wiss. Wien*, 100, 29.
- Tsukahara, N. (1964) Dioctahedral chlorite from the Furutobe mine, Akita prefecture, Japan. *Clay Science*, 2, 56–75.
- Tsuzuki, Y., and Honda, S. (1977) Three examples of Mg-Al chlorite from Kuroko deposits. *J. Mineral. Soc. Japan*, 13, 85–93.
- Vidal, O., Parra, T., and Trotet, F. (2001) A thermodynamic model for Fe-Mg aluminous chlorite using data from phase equilibrium experiments and natural pelitic assemblages in the 100 degrees to 600 degrees C, 1 to 25 kb range. *American Journal of Science*, 301, 557–592.
- Vidal, O., Parra, T., and Vieillard, P. (2005) Thermodynamic properties of the Tschermak solid solution in Fe-chlorite: Application to natural examples and possible role of oxidation. *American Mineralogist*, 90, 347–358.
- Vidal, O., De Andrade, V., Lewin, E., Muñoz, M., Parra, T., and Pascarelli, S. (2006) P-T-deformation-Fe³⁺/Fe²⁺ mapping at the thin section scale and comparison with XANES mapping: application to a garnet-bearing metapelite from the Sambagawa metamorphic belt (Japan). *Journal of Metamorphic Geology*, 24, 669–683.
- Vidal O., Lanari P., Munoz M., Bourdelle F. & de Andrade V. (2016) Deciphering temperature, pressure and oxygen activity conditions of chlorite formation. *Clay Minerals*, in press, DOI: 10.1180/claymin.2016.051.4.06.

- Vrublevskaja, Z.V., Delitsin, I.S., Zvyagin, B.B., and Soboleva, S.V. (1975) Cookeite with a perfect regular structure, formed by bauxite alteration. *American Mineralogist*, 60, 1041–1046.
- Weaver, C.E., Wampler, J.M., and Pecuil, T.E. (1967) Mössbauer Analysis of Iron in Clay Minerals. *Science*, 156, 504–508.
- Wiewiora, A., and Weiss, Z. (1990) Crystallochemical classifications of phyllosilicates based on the unified system of projection of chemical composition; II, The chlorite group. *Clay Minerals*, 25, 83–92.
- Wilke, M., Farges, F., Petit, P.-E., Brown, G.E., and Martin, F. (2001) Oxidation state and coordination of Fe in minerals: An Fe K-XANES spectroscopic study. *American Mineralogist*, 86, 714–730.
- Zazzi, Å., Hirsch, T.K., Leonova, E., Kaikkonen, A., Grins, J., Annersten, H., and Edén, M. (2006) Structural Investigations of Natural and Synthetic Chlorite Minerals by X-Ray Diffraction, Mössbauer Spectroscopy and Solid-State Nuclear Magnetic Resonance. *Clays and Clay Minerals*, 54, 252–265.
- Zhang, G., Burgos, W.D., Senko, J.M., Bishop, M.E., Dong, H., Boyanov, M.I., and Kemner, K.M. (2011) Microbial reduction of chlorite and uranium followed by air oxidation. *Chemical Geology*, 283, 242–250.
- Zheng, H., and Bailey, S.W. (1989) Structures of intergrown triclinic and monoclinic IIb chlorites from Kenya. *Clays and Clay Minerals*, 37, 308–316.