Lithos 178 (2013) 186–196

Contents lists available at ScienceDirect

Lithos

journal homepage: www.elsevier.com/locate/lithos

Tschermak's substitution in antigorite and consequences for phase relations and water liberation in high-grade serpentinites

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ARTICLE INFO

Article history:
Received 14 November 2012
Accepted 4 February 2013
Available online 15 February 2013

Keywords:
Antigorite
Tschermak's exchange
Geothermobarometry
Serpentinite
Dehydration
Subduction zones

ABSTRACT

A model for the incorporation of alumina in FeO–MgO–Al_2O_3–SiO_2–H_2O (FMASH) serpentinites has been developed by considering ideal Tschermak ($Al_2Mg_{-1}Si_{-1}$) solid solution in antigorite. The antigorite model has been calibrated by fitting the experimental conditions for the decomposition of antigorite to chlorite + olivine + orthopyroxene + fluid in the FMASH system. The antigorite Al-contents predicted with this model are in agreement with natural observations and suggest a maximum alumina solubility in antigorite of 3.6 wt.% Al_2O_3 at 20 kbar–650 °C and of 4.5 wt.% Al_2O_3 at 3 kbar–560 °C. In the assemblage antigorite–olivine–chlorite–fluid, the Al-content of antigorite is buffered and temperature sensitive. This temperature sensitivity is the basis for a serpentinite geothermometer at greenschist, amphibolite and eclogite facies conditions. The buffered assemblage is stable in harzburgite compositions for relatively moderate amounts of Al_2O_3 (>1.8 wt.%) and is widespread in lherzolites, where it occurs together with diopside or, in a narrow temperature field, with tremolite.

1. Introduction

Serpentinites are the main carriers of water in the subducted slab and the dehydration reaction of antigorite is a fundamental process in the production of arc lavas (Schmidt and Poli, 1998; Ulmer and Trommsdorff, 1995). Serpentinites in the forearc mantle wedge act as a rheologically weak zone and play a role in decoupling the slab from the mantle (Angiboust et al., 2012; Hilairet and Reynard, 2009; Reynard, 2013). Furthermore, serpentinites are important for exhumation and preservation of high-pressure rocks (Agard et al., 2009; Gerya et al., 2002; Hermann et al., 2000; Malatesta et al., 2012). Current thermophysical models (e.g. Gerya et al., 2002; Hacker et al., 2003; van Keken et al., 2011) of subduction zones processes are based on a thermodynamic model of antigorite (Rüpke et al., 2004) that does not account for the solution of trivalent cations. In particular, trivalent aluminum is thought to have a significant influence on the stability of antigorite (Bromiley and Pawley, 2003; Ulmer and Trommsdorff, 1999). In antigorite, aluminum is believed to be incorporated through a coupled exchange where a Mg and a Si cations are substituted by two Al cations (i.e., Tschermak's exchange). The goal of this work is to develop a thermodynamic model for the Tschermak's exchange in antigorite and, thereby, improve the accuracy of subduction zone phase equilibrium modeling.

The MgO–SiO_2–H_2O (MSH) system is a good first order approximation for metamorphosed ultramafic rocks. The pressure and temperature stability of serpentine minerals has been investigated in this system and has been shown to be of importance for understanding their role in many geological processes (O'Hanley, 1996 and this special volume). Phase relations in the MSH system were established at low pressure by early experimentalists (cf. Bowen and Tuttle, 1949). However, it was recognized that the crystallographic structure and stability of MSH serpentine minerals is sensitive to minor amounts of exotic components. It is known that the substitution of trivalent cations in phyllosilicates such as lizardite (Caruso and Chernosky, 1979; Chernosky et al., 1988; Viti and Mellini, 1997) or phlogopite (Bucher-Nurminen, 1988) increases their stability field by reducing the misfit between the octahedral and tetrahedral sheets. A similar effect is expected for antigorite but its modular structure (i.e. reversal of the tetrahedral layer polarity), which thought to be dependent on composition, pressure, temperature and strain (Auzende et al., 2002, 2006; Mellini et al., 1987; Uehara and Shirozu, 1985; Wunder et al., 2001), makes this picture far more complex.

Fe–Mg partitioning between the ferromagnesian silicates in meta-ultramafic rocks produces that univariant reactions are transformed in divariant fields with a typical temperature interval of ca. 5–10 °C

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http://dx.doi.org/10.1016/j.lithos.2013.02.001

when the system is extended to FMSH composition. Apart from this limited effect, the incorporation of iron into the system is insufficient to create new topologies (O'Hanley, 1996; Trommsdorff and Evans, 1974; Ulmer and Trommsdorff, 1999; Worden et al., 1991). On the contrary, trivalent cations such as aluminum are strongly partitioned in chlorite and antigorite and therefore create new topologies in the MASH systems and produce a more prominent shift of the reactions (ca. 30–40 °C, Bromiley and Pawley, 2003).

Wunder and Schreyer (1997, their Fig. 7), Wunder (1998, his Fig. 6) and Ulmer and Trommsdorff (1995 their Fig. 1; 1999, their Figs. 6 and 9) made the most comprehensive studies of the phase relations in MSH system for ultramafic compositions at high pressure. Ulmer and Trommsdorff (1999) also discussed phase relations in the MASH system but these were limited to those involving only chlorite at temperature conditions higher than those for antigorite stability. Discrepancies in the thermal stability of the antigorite among these studies were attributed to differences in the amounts of various trivalent cations (mainly Al but also Cr) present in the antigorite natural starting material (Bromiley and Pawley, 2003). A full understanding of serpentinite phase relations in the MASH system and a quantitative knowledge of the effect of trivalent cation substitution in antigorite is necessary to improve the modeling of the conditions for dehydration reactions and mineral proportions in subduction zones.

It has been suggested that the Al-content in antigorite coexisting with chlorite and olivine is sensitive to temperature (Eggler and Ehmann, 2010; Li et al., 2004; Padrón-Navarta et al., 2008, 2011; Schwartz et al., 2013) and is thus a potential geothermometer for serpentinite. Geothermobarometry in serpentinite is traditionally hampered by the lack of assemblages buffering the antigorite composition, with the exception of the Fe–Mg exchange between antigorite and olivine (Evans et al., 2012). Therefore, serpentinite geothermobarometry customarily relies on the conditions at which breakdown reactions occur of phases like brucite, diopside or titanian clinohumite (which are, approximately, univariant and pressure independent) and/or alternatively on associated mafic assemblages (e.g. Scambelluri et al., 1995). Recently, Rebay et al. (2012) addressed how the pressure and temperature conditions of high-grade serpentinite could be constrained from mineral compositions in ultramafic assemblages. However, the proposed approach is based on Fe–Mg exchange between antigorite and other minerals and the Ca content in diopside, which are not very sensitive to changes in PT and hence are difficult to calibrate. The Al-content in antigorite may provide an independent constraint of the PT conditions for serpentinite phase equilibria. Such information would permit more precise estimation of the conditions for the subduction and exhumation structures recorded in serpentinite during orogenic cycles (Debret et al., 2013; Hermann et al., 2000; Rebay et al., 2012). Additionally, the relation between the Al-content and the modular structure in antigorite could be investigated more precisely without the need of indirect temperature constraints based on associated mafic rocks (cf. Auzende et al., 2006).

In this work, we compute Al isopleths in antigorite in different mineral assemblages as a function of pressure and temperature. This has been accomplished by considering a Tschermak's substitution in the extended ultramafic CFMASH system. The utility of this solid solution model is then discussed using serpentinite samples from the Betics (Cerro del Almirez, Spain) and the Western Alps (Zermatt-Saas), where metamorphic pressure–temperature conditions are well constrained. We will discuss the implications of the improved antigorite solution model for determining metamorphic conditions in serpentinites and for water liberation during subduction.

2. Tschermak's substitution in antigorite

2.1. Natural observations

Trivalent cations (Al, Cr and Fe^{3+}) are commonly present in antigorite (e.g. Uehara and Shirozu, 1985), aluminum being the most abundant by far (for a recent review of the ferric iron content in antigorite the reader is referred to Evans et al., 2012). Antigorite analyses were compiled to establish the mechanism of Al substitution (Fig. 1a). The analyses were normalized to 116 oxygens, corresponding to a polysome with $m = 17$; where m is the number of tetrahedra spanning a wavelength along the lattice parameter *a*. This definition of the formula unit results in the general formula $M_{3m\text{-}3}T_{2m}O_{5m}(OH)_{4m\text{-}6}$ (e.g. Mellini et al., 1987), where M and T represent the octahedral and tetrahedral sites respectively. For $m = 17$, which is considered the most representative polysome for antigorite in well crystallized serpentinites (e.g. Mellini et al., 1987), the antigorite formula for the MSH endmember is therefore $M_{48}T_{34}O_{85}(OH)_{62}$. The observed trends are compatible with a Tschermak's type substitution ($^{[6]}M^{2+} + {}^{[4]}Si^{4+} = {}^{[6]}Al^{3+} + {}^{[4]}Al^{3+}$), where M^{2+} are divalent cations in the octahedral site (Mg, Fe, Mn and Ni, solid line in Fig. 1). Antigorite used in experimental studies (Fig. 1b) also plots on the tieline joining the antigorite MSH and MASH endmembers (atg and atgts respectively, white stars in Fig. 1, see below) with the exception of the antigorite used by Wunder and Schreyer (1997), most probably this anomaly is the effect of a large ferric iron content (1.09 wt.% Fe_2O_3). Therefore, in general, compositional data provide evidence that Al incorporation into antigorite can be described as a first approximation by the Tschermak's substitution.

2.2. Implications for the MASH compositional system

The addition of the Al_2O_3 component to the simple MSH system results in a pressure–temperature dependency of the Tschermak substitution in antigorite that modifies the MSH phase relations (Fig. 2a). The effect on the MSH phase relations can by illustrated by considering, for simplicity, Tschermak's exchange only in antigorite (Fig. 2). Talc, dense hydrous magnesium silicates (DHMSs) and humite series have been not included for simplicity. The qualitative phase relations in a Schreinemakers P–T projection (Fig. 2b) show the new invariant point possible in the four component MASH system that relates the six phases clinochlore, forsterite, enstatite, fluid, pyrope and antigorite (the latter spanning its composition from atg to atgts, Fig. 2a). The arrangement of the reactions and the location of this invariant point (ca. 60 kbar and 570 °C) were deduced experimentally by Bromiley and Pawley (2003) (their Fig. 2, although they did not consider the fluid absent reaction, [H_2O], our Fig. 2b).

In the MSH system, all phases are considered to have fixed stoichiometry so the only reactions are univariant (thin line in Fig. 2b). The introduction of Al into the system leads to the complication that phase compositions change as a function of pressure and temperature. Apart from clinochlore and pyrope (Fig. 2), the only phase that incorporates substantial amounts of Al (disregarding enstatite, but see Fockenberg and Schreyer, 1997) is antigorite. Al-content in antigorite changes continuously as a function of pressure, temperature and bulk composition (i.e. Al-isopleths, Fig. 2c) in the MASH system. To visualize these changes we arbitrary divide the antigorite solid solution into *pseudocompounds*, the conceptual basis for Gibbs free energy minimization in Perple_X (Connolly, 1990). In the case of antigorite, this involves a series of discrete compositions along the tieline joining the atg and atgts endmembers, that are labeled as low-Al antigorite and high-Al antigorite in a relative way. A practical consequence of the *pseudocompound* approach is that the continuous PT compositional changes in antigorite result in *pseudounivariant* reactions and *pseudoinvariant* points (dashed lines and black dots in Fig. 2c). For the definition of all these terms the reader is referred to Connolly (1990). The PT dependence of the Al-isopleths in antigorite is controlled by the buffering assemblage along the *pseudounivariant* reactions (e.g. [fo, en] is pressure dependent whereas [prp, en] is temperature dependent) (Fig. 2c). Of particular relevance for common serpentinite compositions is the *pseudounivariant* reaction [prp, en]:

$$\mathrm{Atg(low-Al) + clin = Atg(high-Al) + fo + H_2O.} \quad (1)$$