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Physical properties of CaAl₂Si₂O₈–CaMgSi₂O₆–FeO–Fe₂O₃ melts: Analogues for extra-terrestrial basalt

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ABSTRACT

The effects of increasing quantities of iron on the viscosity, heat capacity and density of a haplobasaltic base composition (anorthite-diopside 1 atm eutectic) were determined. Super-liquidus viscosity and density were measured in air using the concentric cylinder method and double-bob Archimedean method, respectively. Low-temperature viscosities were measured using the micropenetration method for the melts that could be quenched to glasses. The effect of iron oxidation state on viscosity was investigated above the liquidus under reduced fO_2 and at the glass transition temperature from quenched samples of varying redox state. Iron significantly decreases the melt viscosity, especially near the glass transition and lowers the activation energy at low temperature. Density increases with addition of iron and the experimental measurements are in good agreement with predictions of existing models. The reduction of Fe³⁺ to Fe²⁺ produces a slight viscosity decrease at high temperature but affects properties near the glass transition more strongly. Thus, for iron-rich compositions, the redox state must be taken into account to obtain accurate estimates of the physical and thermodynamic properties, especially at low temperatures. As a result, the iron-bearing anorthite-diopside system approaches the viscous behaviour of terrestrial and extraterrestrial basaltic compositions and then appears to be good analogue for basaltic systems. At magmatic temperatures, the viscosity difference between common terrestrial basalt and lunar or Martian basalt is estimated to be 0.5 to 1 order of magnitude. Although these results are consistent with inferences drawn from planetary observations on the fluidity of lunar and Martian lava flows, the crystallisation sequence of such systems will need to be investigated to improve interpretation of lava flow morphologies.

1. Introduction

The physico-chemical processes behind magmatic and volcanic phenomena (including partial melting, crystallisation, degassing, fragmentation and explosive eruption) are governed by transport dynamics and by magma properties, which determine the extent and efficiency of energy, momentum and mass exchange between phases in multiphase magmatic mixtures (Papale, 1999; Sparks, 2003). The viscoelasticity (e.g., viscosity and elastic moduli), together with the density, control the fluid dynamics of transport and the buoyancy forces, respectively. The thermodynamic properties (enthalpy, entropy, and volume) and their P–T derivatives (specific heat capacity, compressibility, and thermal expansivity) provide information about the energy budget of the magmatic mixtures and define the thermodynamic state of the system (e.g., Richet, 1987). To identify and quantify the physical mechanisms dominating magmatic and volcanic processes, and their impact on the environment, a robust comprehensive experimental description of the physico-chemical properties, together with the application of modelling, is required to evaluate and forecast the evolution of such processes.

To date, despite a considerable number of experimental studies (e.g., Mysen et al., 1984; Dingwell and Virgo, 1987, 1988; Lange and Carmichael, 1987; Dingwell and Brearley, 1988; Toplis et al., 1994; Richet and Bottinga, 1995; Magnien et al., 2004; Solvang et al., 2004; Webb., 2005; Richet, 2009) and modelling (Russell et al., 2002, 2003; Giordano and Dingwell, 2003a; Hui and Zhang, 2007; Giordano et al., 2008a; Kondratiev et al., 2008), the chemical and structural role of iron in silicate melts still remains incomplete (Wilke, 2005). The situation is especially critical for iron-rich volcanic products, which are particularly experimentally challenging.

In both melts and crystals, iron may be found in a variety of coordination environments ranging from tetrahedral (^{IV}Fe), to pentahedral (^VFe), to octahedral (^{VI}Fe) (Mysen et al., 1984; Giuli et al., 2003; Wilke et al., 2007) and it can occur either as a reduced, ferrous (Fe²⁺), or oxidised, ferric (Fe³⁺) component. The oxidation state of iron (i.e., Fe²⁺/Fe_{tot}) describes the redox state of the magma (Christie et al., 1986; Carmichael, 1991; Herd, 2008) and represents

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a first-order influence on the crystallisation sequence of phases and on resultant degassing (Brooks et al., 1991; Toplis and Carroll, 1995; Lattard and Partzsch, 2001; Moretti and Papale, 2004). Iron is the most abundant transition metal present in the terrestrial planets and a major element in basaltic melts that volumetrically dominate (~95 vol.%) the erupted products at the Earth's surface and presumably those of other terrestrial planets (e.g. Mars; Boynton et al., 2007; Baratoux et al., 2011). The proportion of iron within crustal rocks reflects the composition and degree of partial melting of the protolith of the parental magma, providing information about the thermal state and thereby evolution of planetary mantles (e.g., Herzberg et al., 2010; Baratoux et al., 2011).

On Earth, the iron content (FeO_{tot}) of magma commonly ranges between 3 and 12 wt.% (Manson, 1967). Remarkable iron-rich compositions (12-16 wt.% FeO_{tot}) do exist but are rare, typically associated with ultrabasic rocks in large igneous provinces (e.g., ferropicrite in Parana-Etendeka and Siberia) (Francis et al., 1999; Gibson et al., 2000); or exhibited by low-silica effusive rocks such as ultramafic Komatiitic lavas (Arndt et al., 1977); or found in hot spot related volcanic provinces, e.g., Hawaii, Galapagos, Craters of the Moon lava field, Iceland (Fisk et al., 1982; Stout et al., 1994; Norman and Garcia, 1999; Eason and Sinton, 2009). Extremely high iron contents (up to 22 wt.% FeOtot) were inferred for the majority of the volcanic products of both Mars and the Moon (Binder, 1976; Gellert, 2004; Boynton et al., 2007). The composition and the morphology of both terrestrial ultrabasic flows and Martian and lunar volcanic landforms suggest fast eruption rates, high eruption temperatures and very low viscosity magmas (e.g. Huppert and Sparks, 1985; Cas et al., 1999; Baratoux et al., 2009; Hauber et al., 2009: Vaucher et al., 2009).

Here we investigated the physical properties of the anorthitediopside (CaAl₂Si₂O₈-CaMgSi₂O₆) eutectic composition at 1 atm with additional amounts of iron (5, 10, 20, and 30 wt.% Fe₂O₃). Anorthitediopside eutectic composition was selected because its physicochemical properties are well characterised and it has long been considered a suitable analogue for basaltic composition (Scarfe et al., 1983) with only minor restrictions (Giordano et al., 2008b). This study combines viscometric, calorimetric and volumetric measurements to address the rheological and thermodynamic description of iron-rich melts that may serve as analogues for extra-terrestrial volcanic products. We show that with the addition of iron, the anorthite-diopside eutectic approximates the inferred rheological behaviour of lunar and presumably Martian basalts.

2. Experimental methods

2.1. Starting material

Five batches of synthetic anorthite–diopside eutectic composition $(An_{42}Di_{58}: AD)$ were synthesised from oxides and carbonate powders, previously dried at 120 °C for 24 h. Each batch was fused in a platinum crucible for 2 h at 1873 K. The melts were poured onto a

stainless steel plate for cooling and the resulting glasses were finely ground. Pure iron oxide powder was added to the individual batches to provide samples containing 5, 10, 20 and 30 wt.% Fe₂O₃, named AD-5, AD-10, AD-20 and AD-30, respectively. The mixtures were melted for 3 h at 1873 K in platinum crucibles that were previously doped with iron to minimise the iron loss to the crucible wall. In order to eliminate bubbles and promote homogenisation, each melt was stirred for 24 h using a rotational viscometer. Sample compositions of the homogenised samples are presented in Table 1.

2.2. High-temperature viscometry in air

High-temperature viscosity of the dry liquid samples was determined by cooling in 25 K increments via the concentric cylinder method (Dingwell, 1986). The apparatus consists of a Deltech furnace heated by MoSi2 elements and a Brookfield rheometer model RVTD III Ultra (Rotary Variable Transducer Displacement) with a full range torque of 7.2×10^{-4} N·m. Instrument drift was checked by reacquisition of the highest temperature data-point at the end. The precision on the viscosity for this apparatus was derived from replication of viscosity determination of standard melt NBS SRM 711 standard lead-silica glass and is estimated at \pm 3% at the 2 σ (Dingwell, 1986). The temperature calibration was determined by the immersion of a S-type (Pt/Pt₉₀-Rh₁₀) thermocouple into the melt over a large range of temperatures. After measurements, the melts were poured onto a stainless steel plate to quench large samples used for micropenetration experiments. For AD-20 and AD-30, those large samples showed extensive crystallisation, preventing for further analysis.

2.3. Loop fusion and high-temperature viscometry under reduced conditions

The role of iron oxidation state on viscosity at high temperature was investigated for the iron-rich melts AD-10 and AD-20. The measurements were acquired with the same concentric cylinder technique, but using a vertical alumina muffle tube furnace equipped with a CO₂-CO gas-mixing line. The top of the furnace was fitted with an iris diaphragm to allow the spindle to pass through (Dingwell and Virgo, 1987). At isothermal conditions, the melt was initially equilibrated in air and then reduced using mixed CO₂–CO gas flows within the muffle tube. The oxygen fugacity was monitored with a differential voltmeter linked to a yttria-stabilised zirconia oxygen sensor placed just below the crucible. Several oxidation states were achieved by changing the CO2:CO ratio. At each reduction step at least 24 h was required to permit melt equilibration (i.e., time invariant viscosity record). After the last step (i.e. the most reduced condition) the gas flow was shut off and the melt oxidised to reacquire the initial condition in equilibrium with air. Sampling was performed after each equilibration by a "dip quench" technique that consisted of inserting an alumina-oxide rod into the melt which was then withdrawn and

 Table 1

 Chemical compositions in wt.% (average of 5 to 10 electron microprobe analyses for each sample) and normalised mol%.

Sample	AD		AD-5		AD-10		AD-20		AD-30	
	wt.%	mol%	wt.%	mol%	wt.%	mol%	wt.%	mol%	wt.%	mol%
SiO ₂	49.23 (0.47)	50.12	47.39 (0.26)	49.24	45.64 (0.21)	48.82	40.42 (0.19)	46.48	35.87 (0.62)	44.10
Al ₂ O ₃ Fe ₂ O _{2tot} ^a	14.96 (0.07) 0.00	8.98	14.22 (0.11) 5.06 (0.16)	8.71 1.98	13.52 (0.1) 9.03 (0.09)	8.53 3.64	11.93 (0.1) 20.20 (0.17)	8.08 8.74	10.35 (0.11) 29.93 (0.82)	7.50 13.84
MgO	10.01 (0.1)	15.20	9.76 (0.08)	15.12	9.24 (0.06)	14.74	8.12 (0.06)	13.92	6.3 (0.12)	11.54
CaO	23.57 (0.2)	25.71	22.41 (0.17)	24.95	21.18 (0.14)	24.28	18.49 (0.12)	22.78	17.47 (0.45)	23.02
Total	97.77	100	98.84	100	98.61	100	99.17	100	99.92	100

Numbers in brackets are the associated standard deviation.

a Total iron as Fe₂O₃.

plunged into distilled water to ensure a rapid quench. Although the action was performed as quickly as possible, some melts may have undergone some oxidation during the process.

The effect of iron oxidation state on viscosity was not measured for AD-5 at high temperature; instead samples were reduced via loop fusion experiments under controlled fO_2 . Approximately 30 mg of glass sample were suspended on a platinum wire loop within a similar vertical alumina muffle tube furnace tightly capped and equipped with a CO₂–CO gas-mixing facility. After 24 h at isothermal condition, when the sample reached equilibrium with the surrounding atmosphere, the platinum wire was severed, dropping the sample into distilled water to quench. The temperature and fO_2 were monitored continuously using a S-type thermocouple and a yttria-stabilised zirconia oxygen sensor placed together close to the sample.

Glass chips resulting from these experiments were mounted as polished sections for petrographic and chemical analysis carried out with a CAMECA SX 100 Electron MicroProbe Analyser (EMPA) at the University of Munich using an accelerating voltage of 15 kV and a beam current of 20 nA, with counting time of 5 s for the background and 10 s for the elements. The standards used were wallastonite for Si and Ca, albite for Al, hematite for Fe and periclase for Mg. The data were corrected according to the PAP procedure (Pouchou and Pichoir, 1985). Samples were also used for determination of Fe²⁺/Fe_{tot} ratio by potassium dichromate titration and to accomplish calorimetric measurements (see following methods).

2.4. Low temperature viscometry

The low-temperature viscosities were measured using a micropenetration technique. The measurements were accomplished near the glass transition in the range of $10^{8.6}$ to $10^{11.5}$ Pa s using a vertical pushrod Bähr 802 V dilatometer (Hess et al., 1995 and reference within). The present assembly uses hemispherical Ir indenters with a force of 1.2 N, resulting in indentation depth up to 150 to 200 µm. Although this technique requires small amount of material, the samples need to have polished parallel faces. Therefore only samples quenched from pouring melt (equilibrated in air) could be measured. Each measurement was carried out on a different sample under isothermal conditions (15 min after the target temperature was

reached) to insure a fully relaxed state. Analyses were conducted under a sustained Argon atmosphere to avoid further oxidation. Measurements that showed evidence of oxidation or crystallisation were not used.

2.5. Differential scanning calorimetry (DSC) methodology

The glass transition temperature was estimated from calorimetric measurements (Moynihan et al., 1974; Scherer, 1986) using a Differential Scanning Calorimeter (DSC 404 Pegasus from NETZSCH Gerätebau). The samples used here were small glass chips (<50 mg) that resulted from the "dip quench" technique after viscosity measurements or loop fusion experiments. After initial heating into the liquid field (i.e., approximately 50 K above the glass transition temperature), the samples were exposed to four cycles of cooling and subsequent heating at a fixed rate of 20, 15, 10 and 5 K/min. For each sample and each rate, individual heat capacity (C_p) curves were measured against a sapphire of the equivalent mass. The time spent above the glass transition was minimised to reduce the occurrence of crystallisation or oxidation. The reproducibility of the C_p curves obtained is a clear indication that no significant degradation of the samples occurred.

From the C_p curves, the limiting fictive temperature (T_f') describing at which temperature the liquid structure is frozen in, was determined according to the method of Moynihan, 1995 (Fig. 1). In order to compare the peak shape of all runs, temperatures were also collected at the onset of the peak (T^{onset}_g), at the maximum value of the peak (T^{peak}_g) and at the onset of the stable liquid heat capacity (T^{fuuid}_g) (Fig. 1). The reproducibility of the run and instrument deviation lead to a temperature deviation of ± 3 °C.

2.6. High temperature densitometry

The liquid densities were determined from approximately 200 K above the liquidus by cooling in 50 K increments via the double-bob Archimedean technique following the method of Bockris et al. (1956). The apparatus used here and the precision of this technique (<0.2%) has been previously described in Dingwell et al. (1988). The balance employed was a digital model Mettler® AE100 that was positioned above the alumina muffle tube furnace. The temperature of



Fig. 1. Example of heat capacity (C_p) curves for AD-10 at various cooling rates. The left high inset shows the method to collect the $T_{f'}$ and T_g values at the onset, peak and liquid position. Tf' is defined as the upper temperature limit required for the area I to be equal to area II. The bottom right inset is the variation of the different temperature values as a function of cooling rate.



Fig. 2. Iron redox state as a function of oxygen fugacity for the set of samples AD-10 obtained by potassium dichromate titration. The full line is the linear trend of the data, the dotted line represents the estimation according to the model of Kress and Carmichael (1991) and the dashed line according to the model of Moretti (2005).

the sample was previously calibrated by inserting a S-type thermocouple directly into the melt over a large range of temperature. Temperature uncertainties, including contributions from thermal gradients and time fluctuations, are estimated to contribute an imprecision of less than 0.1% to the experimental density data, since the thermal expansivities of the samples are small (Courtial and Dingwell, 1999). The measurements were conducted at least 30 min after isothermal equilibrium in a set of three immersions for the two bobs in order to compute a mean and standard deviation of the replicate buoyancy determinations (Courtial and Dingwell, 1999).

2.7. Samples redox state

The oxidation state of each investigated glass was determined by potassium dichromate titration, a wet-chemistry method based on a simple potentiometric titration (Giuli et al., 2011). Approximately 30 mg of finely ground glass is first digested with sulphuric and hydrofluoric acid under CO₂ atmosphere. The solution is then titrated with a potassium dichromate oxidant. The potential values during titration were recorded automatically and directly converted to Fe²⁺ concentration. Finally the Fe²⁺/Fe_{tot} ratio is calculated from the total iron content obtained from EMPA measurements. As described in Bezos and Humler (2004) care has to be taken during the wet-chemistry procedure to avoid irreversible oxidation of ferrous iron. The standard deviation of the measurements was determined to be 1.3% based on ten titration measurements of the certified standard BHVO-1. The Fe^{2+}/Fe_{tot} values for the set of AD-10 samples reduced under controlled atmosphere are reported in Fig. 2 as a function of fO₂ and compared with the model of Kress and Carmichael (1991) and Moretti (2005). We note that the Fe^{2+}/Fe_{tot} values for melts that were quenched from low fO2 are too "oxidised" relative to the models. In contrast, the agreement is very reasonable for samples quenched from melts equilibrated in air. Samples quenched from lower fO2 could be affected by oxidation during the quenching process and during the digestion of the sample in solution.

3. Results

3.1. High temperature viscosity

The high-temperature viscosities measured in air with the concentric cylinder are presented in Fig. 3, and reported in Table 2. Liquidus temperatures for the samples AD-10, AD-20 and AD-30



Fig. 3. Temperature dependence of viscosity measured in air using the concentric cylinder and micropenetration methods. The low temperature viscosities for AD-20 were obtained using viscosity estimation at $T_{t'}$ using Eq. (2). The viscosity of AD-30 at low temperature could not be obtained. The bold lines are the TVF fit calculated from Eq. (3).

Table 2

High- and low-temperature viscosities measured in air, respectively with the concentric cylinder and micro penetration (except for AD-20, see Section 3.3).

T (K)	$\log \eta (Pa \cdot s)$						
	AD	AD-5	AD-10	AD-20	AD-30		
1867	-0.14	-0.30	-0.45	-0.71	-1.03		
1842	-0.06	-0.22	-0.39	-0.66	-0.98		
1818	0.02	-0.15	-0.32	-0.60	-0.93		
1793	0.10	-0.08	-0.25	-0.54	-0.87		
1769	0.18	0.00	-0.18	-0.48	-0.82		
1744	0.27	0.08	-0.10	-0.41	-0.75		
1719	0.36	0.16	-0.01	-0.34	-0.69		
1695	0.45	0.25	0.07	-0.26	-0.62		
1670	0.56	0.35	0.17	-0.18	-0.55		
1646	0.67	0.46	0.27	-0.09	-		
1621	0.79	0.57	0.38	0.01	-		
1596	0.92	0.69	0.49	0.11	-		
1572	1.06	0.83	0.61	0.21	-		
1547	1.18	0.97	0.74	-	-		
1523	1.35	1.10	0.88	-	-		
1498	1.52	1.27	1.04	-	-		
1473	1.70		-	-	-		
1090	8.59	-	-	-	-		
1070	9.34	-	-	-	-		
1054	9.97	-	-	-	-		
1029	11.07	-	-	-	-		
1018	11.46	-	-	-	-		
1061	-	8.63	-	-	-		
1048	-	9.12	-	-	-		
1036	-	9.62	-	-	-		
1020	-	10.23	-	-	-		
1019	-	10.25	-	-	-		
1004	-	10.90	-	-	-		
1042	-	-	8.63	-	-		
1024	-	-	9.33	-	-		
1003	-	-	10.04	-	-		
984	-	-	11.03	-	-		
951	-	-	-	12.11 ^a	-		
950	-	-	-	11.81 ^a	-		
949	-	-	-	11.64 ^a	-		
948	-	-	-	11.51 ^a	-		

^a Viscosity values are calculated at T_f'.



Fig. 4. Isothermal viscosity variation as a function of the bulk molar fraction of total iron expressed as Fe_2O_3 .

were indirectly observed to be as high as 1498 K, 1572 K and 1670 K, respectively; below those temperatures clear onsets of crystallisation were inferred from the sudden increase of the measured viscosity. Regardless of the redox state, the isothermal viscosity variations show that the addition of 20 wt.% iron (8.7 mol% Fe₂O₃) causes a decrease of 1 log unit at 1470 K (Fig. 4). The data were first fitted within the same temperature interval (1867 to 1670 K) using an Arrhenian relationship:

$$\ln \eta = A_A + \frac{\Delta H_\eta}{RT} \tag{1}$$



Fig. 5. Enthalpy variation (ΔH_{η}) calculated from Eq. (1) in the high and low temperature interval as a function of the bulk molar fraction of iron expressed as Fe₂O₃. The ΔH_{η} LT for AD-20 (grey diamond) was calculated from the TVF equation.

where η is the viscosity, A_A a pre-exponential term, ΔH_{η} the enthalpy variation equivalent to activation energy of viscous flow, R the ideal gas constant and T the temperature. Although the Arrhenian relationship is invalid over a large temperature range (e.g., Hess et al., 1995; Richet and Bottinga, 1995; Whittington et al., 2001; Russell et al., 2002, 2003) this approximation is suitable for data comparison over limited temperature or viscosity ranges. The terms of Eq. (1) are presented in Table 3 together with their root mean square error (hereafter RMSE). Fig. 5 shows the linear decrease of the high-temperature ΔH_{η} from 210 kJ/mol for the iron-free AD sample to 145 kJ/mol for the iron-rich AD-30 sample (equivalent to 31% decrease).

The results of the superliquidus viscosity measurements under varying controlled oxygen fugacity, together with the corresponding melt redox states are reported in Table 4. The maximum decrease of viscosity due to iron reduction in AD-10 and AD-20 is 0.03 log Pa s and 0.12 log Pa s, respectively.

3.2. Low temperature viscosity

The low-temperature viscosities measured by micropenetration are presented in Fig. 3 and reported in Table 2. The low-temperature viscosities presented here for sample AD-20 were inferred from the calorimetric glass transition (see Section 3.3). For sample AD-30, neither micropenetration nor calorimetric measurements on a pure glass sample could be obtained because of widespread crystallisation during quenching. The addition of 20 wt.% of iron causes a viscosity drop of 3 orders of magnitude at 1070 K (Fig. 4). The data were fitted with Eq. (1) within the viscosity interval of the measurements $(10^{8.6} \text{ to})$ $10^{11.5}$ Pa s); and for AD-20, ΔH_{η} LT was estimated within the same range from the non-Arrhenian fit obtained in Section 3.4 (Table 3). As iron is added to the base composition ΔH_n LT decreases non-linearly between iron-free AD and AD-10 (Fig. 5); the addition of 5 wt.% of iron to the iron-free composition causes a decrease of 47 kJ/mol, and additional 5 wt.% induces a lesser decrease of 18 kJ/mol. An addition of further 10 wt.% yields a large increase in the enthalpy variation; the ΔH_n LT for AD-20-S1 is estimated to be 962 kJ/mol.

3.3. The calorimetric glass transition temperatures and derived viscosity

The temperatures measured at the calorimetric glass transition, including the limiting fictive temperature (T_{f}') , the onset (T_{g}^{onset}) and the maximum peak (T_g^{peak}) temperatures, and the onset of the liquid field (T^{liquid}) are listed in Table 5 for each (oxidised and reduced) composition. The Tg^{liquid} of the AD-20 sample equilibrated in air (AD-20-S1) could not be obtained because of the occurrence of crystallisation after crossing of the glass transition, which prevented reproducible measurements on the same sample. For this sample, T_f was calculated from its linear correlation with $T_{\rm g}^{\rm onset}$ obtained from the other measurements ($T_{f}' = 0.964 T_{g}^{onset} + 32.83$; $R^2 = 0.981$). In contrast, the reduced samples ($Fe^{2+}/Fe_{tot} > 0.3$) are more "stable", with no crystallisation taking place immediately above Tg; the liquid field could be reached and the measurements were reproducible. The shift of the glass transition temperatures towards lower values as a function of iron content is non-linear, as shown in Fig. 6a. For the most oxidised samples the addition of 10 wt.% iron to the base composition decreases Tf' by 40 K, while an additional 10 wt.% of iron decreases T_f' by only an additional 20 K. For the reduced samples T_f' is shifted to lower values and the glass transition temperature dependence on iron content becomes more linear. The effect of redox state on $T_{f'}$ is dependent on the iron content (Fig. 6b); logically, the more iron the more the redox state affects $T_{f'}$. The increase of Fe²⁺/ Fe_{tot} from 0.16 to 0.50 leads to a decrease of T_{f} by 30 K in AD-20; 10 K in AD-10; and no decrease in AD-5. Upon further iron reduction $(Fe^{2+}/Fe_{tot} > 0.5) T_{f}$ remains constant. Therefore, a minimum T_{f} value is reached at approximately 50% iron reduction.

Table 3

Enthalpy variation calculated at high temperature (ΔH_{η} HT) and at low temperature (ΔH_{η} LT) from Eq. (1), TVF fitting parameters calculated from Eq. (3) and fragility index is calculated from Plazek and Ngai (1991) at Tg=T_{log \eta=12}.

	A _A HT	$\Delta H_{\eta} \text{ HT}$ (kJ/mol)	RMSE ^a	A _A LT	ΔH_{η} LT (kJ/mol)	RMSE ^a	A _{TVF} (log Pa s)	B _{TVF} (log Pa s/K)	C _{TVF} (K)	RMSE ^a	m ^b	SMc	NBO/T ^c
AD	-13.87	210	0.041	-76.20	869	0.078	-4.129	4362	742	0.117	60.40	40.91	0.94
AD-5 (42)	-12.45	183	0.041	-71.90	810	0.062	-4.099	4227	725	0.088	60.58	40.63	0.87
AD-10 (22)	-13.08	183	0.034	-71.62	792	0.270	-4.146	4147	713	0.092	60.95	40.18	0.81
AD-20 (S1)	-12.18	163	0.017	-94.90	962	0.169	-4.125	3829	709	0.167	64.24	39.51	0.66
AD-30	-11.73	145	0.006	-	-	-	-	-	-	-	-	-	-
AD-5 (39)*	-	-	-	-86.83	936	0.177	-4.125	4318	718	0.162	59.37	42.34	0.99
AD-10 (28)*	-	-	-	-80.76	863	0.119	-4.125	4419	686	0.175	56.48	43.44	1.05
AD-20 (S2)*	-	-	-	-93.87	935	0.112	-4.125	3788	692	0.073	63.65	41.42	0.80
AD-20 (S3)*	-	-	-	-92.84	921	0.190	-4.125	3791	687	0.084	63.22	43.41	0.94
AD-20 (S4)*	-	-	-	-91.21	909	0.170	-4.125	3839	684	0.153	62.43	45.46	1.09

* Sample equilibrated under reduced conditions, ΔH_{η} LT is calculated between $\eta = 10^{8.5}$ and 10^{11} Pa s from the TVF equation. ^a Root mean square error.

^b Fragility index.

^c Calculated considering Fe³⁺ to be network former and Fe²⁺ to be modifier.

The viscosity at $T_{f'}$ is estimated considering that the enthalpic relaxation time is identical to that of viscous flow (e.g. Scherer, 1984; Dingwell and Webb, 1990) leading to an equivalence between the cooling rate and the viscosity at $T_{f'}$ via:

$$\log \eta \left(\operatorname{at} \mathbf{T}_{\mathrm{f}}^{\prime} \right) = K - \log |q| \tag{2}$$

where K is a constant, the so called shift factor, and g is the cooling rate. K is calculated using Eq. (1) from the samples that could be measured with the micropenetration technique (AD, AD-5 and AD-10). Although K is sometimes considered independent of composition (Toplis et al., 2001; Sipp and Richet, 2002), other studies have evidenced a non-linear decrease of K with increasing excess oxides (e.g., Gottsmann et al., 2002). Here, K is found to be the same (10.88 ± 0.23) when calculated for AD-5 and AD-10, however, it is 11.2 ± 0.11 when calculated for the iron-free AD composition. Apart from this slight difference, a systematic compositional dependence of K cannot be inferred. Therefore the viscosity at T_{f} was calculated using an averaged K value of 11.04 ± 0.37 . The maximum error on the viscosity is then estimated at $\pm 0.37 \log$ unit. At T_f, iron reduction has a little effect on the viscosity of AD-5 and AD-10 but a larger influence on AD-20 (Fig. 7). In the case of AD-20 near the glass transition, the most reduced melt ($Fe^{2+}/Fe_{tot} = 0.67$) has a viscosity of one order of magnitude lower than the melt equilibrated in air. Further melt reduction, above $Fe^{2+}/Fe_{tot} = 0.5$, does not affect T_g , and hence, not affect the viscosity.

Table 4

Isothermal viscosity measurements obtained under controlled fO_2 for AD-10 at 1623 K and AD-20 at 1658 K. In brackets are the standard deviations of titration measurements calculated from two samples under the same conditions. Sample no. 32 has been collected at the end of the melt reduction steps, once the melt is back in equilibrium with air.

	Sample no.	log fO ₂	$Fe^{2+}/\Sigma Fe$	$\log\eta~(\text{Pa s})$
AD-10	#22	-0.705	0.18 (0)	0.56
	#24	-3.758	0.32 (0.05)	0.54
	#26	-6.301	0.50(0)	0.53
	#28	-7.660	0.73 (0.04)	0.53
	#31	-8.763	0.74 (0.03)	0.54
	#32	-0.674	0.17(0)	0.56
AD-20	#S1	-0.737	0.18(0)	-0.121
	#S2	-3.139	0.36 (0)	-0.198
	#S3	-7.024	0.52 (0.01)	-0.232
	#S4	-9.240	0.67 (0.02)	-0.236

3.4. Viscosity behaviour over the entire temperature range

Looking at the temperature dependence of viscosity over the entire range of investigated temperatures, the data can be fitted using the Tammann–Vogel–Fulcher (TVF) equation (Vogel, 1921; Fulcher, 1925; Tammann and Hesse, 1926a):

$$\log \eta = A_{\rm TVF} + \frac{B_{\rm TVF}}{(T - C_{\rm TVF})} \tag{3}$$

where A_{TVF} represents a lower limit of silicate melt viscosity at high temperature; B_{TVF}, the pseudo-activation energy; and C_{TVF} represents the temperature at which viscosity would become infinite. The employment of this equation is justified by comparison purposes as most of experimental rheological studies of melts relevant to geological studies use this equation. The parameter A_{TVF} is considered as a constant for all silicate melts according to several numerical and theoretical studies (Myuller, 1955; Eyring et al., 1982; Angell, 1985). Because of model optimisation issues, Russell et al. (2003) and Giordano et al. (2008a, 2009) determined that A_{TVF} is approximated to a value of $-4.55 \log Pa s$ for natural and synthetic analogues and Arrhenian to non-Arrhenian silicate liquids. Here, A_{TVF} was estimated from AD, AD-5 and AD-10 to be -4.125 ± 0.4 and input in the TVF equation to estimate B_{TVF} and C_{TVF} for the compositions that could not measured by micropenetration. The fitting parameters, together with the associated uncertainty of the fit are reported in Table 3. The fragility of a melt is commonly used to track departures of viscosity from Arrhenian behaviour and to distinguish strong Arrhenian-like (low fragility values) and *fragile* non-Arrhenian (high fragility values) melts. The fragility index is calculated in terms of the steepness index (m) (Plazek and Ngai, 1991) at $T_g\!=\!T_{\text{log }\eta=12}$ (Table 3). For all melts, oxidised or reduced, the fragility index varies between 56.5 and 64.2. The addition of iron slightly increases the fragility, while it decreases with Fe reduction (Table 3).

3.5. High temperature density measurements

The measured high-temperature densities are given in Table 6 together with their associated relative uncertainties. These, obtained by calculating the standard deviation of duplicate buoyancy measurements, do not exceed 1%. The melt densities range from 2.509 g·cm⁻³ for the base composition to 3.003 g·cm⁻³ for AD-30, and decrease linearly with increasing temperature (Fig. 8). The density values for the iron-free AD eutectic melt are in good agreement with those obtained by Holzapfel et al. (2001). Within the uncertainties, the

Table 5 Limiting fictive temperatures and glass transition temperatures collected at the onset, peak and liquid position of the C_p curves for all oxidised and reduced samples at 5, 10, 15 and 20 K/min cooling/heating rate.

Sample i	no.	$\mathrm{Fe}^{2+}/\mathrm{Fe}_{\mathrm{tot}}$	$T_{f'}(K)$				Tg ^{onset} (K)			T ^{peak} (I	()			Tgliquid (K)		
			q (K/m	iin)			q (K/m	iin)			q (K/m	in)			q (K/m	in)		
			5	10	15	20	5	10	15	20	5	10	15	20	5	10	15	20
AD		-	1001	1006	1012	1018	1001	1011	1013	1014	1034	1042	1048	1053	1049	1059	1067	1072
AD-5	#42	0.17	978	985	990	1001	982	990	989	1002	1015	1024	1028	1039	1031	1042	1049	1059
	#41	0.32	974	983	987	993	981	983	991	994	1012	1021	1026	1030	1029	1038	1048	1053
	#40	0.70	974	983	989	991	981	983	989	993	1012	1019	1026	1029	1029	1038	1045	1052
	#39	0.71	981	989	994	998	982	991	997	1000	1015	1024	1030	1033	1031	1040	1049	1053
AD-10	#22	0.18 (0)	958	967	974	976	961	968	975	978	996	1003	1010	1014	1016	1023	1028	1035
	#24	0.32 (0.05)	956	963	968	973	961	968	971	974	994	1001	1006	1012	1010	1019	1030	1033
	#26	0.50(0)	950	958	965	968	953	962	965	970	989	997	1003	1006	1005	1015	1020	1027
	#31	0.74 (0.03)	956	961	969	972	961	966	971	973	989	998	1003	1010	1008	1019	1023	1029
	#28	0.73 (0.04)	950	962	965	971	958	961	969	968	988	997	1003	1006	1006	1014	1021	1025
AD-20	#S1	0.18 (0)	951 ^a	950 ^a	949 ^a	948 ^a	952	951	950	949	983	981	982	980	997	995	998	995
	#S2	0.36(0)	926	930	932	936	926	933	932	937	960	963	966	970	983	981	984	990
	#S3	0.52 (0.01)	920	924	929	930	917	924	925	930	952	958	966	966	969	981	987	992
	#S4	0.67 (0.02)	918	924	928	932	917	921	926	928	944	954	961	965	1010	1010	1020	1015

^a Calculated from the linear relationship: $T_f = 0.964 T_g^{onset} + 32.83$; $R^2 = 0.981$.

experimental density data are fitted linearly as a function of temperature according to:

$$\rho = a + bT \tag{4}$$



Fig. 6. a) Variation of the glass transition taken at $T_{f'}$ for cooling/heating rate of 10 K/min as a function of the bulk molar fraction of iron. Full symbols represent the values for the samples equilibrated in air (AD-5-42, AD-10-22 and AD-20-S1) and empty symbols for the most reduced samples (AD-5-40, AD-10-28, and AD-20-S4). b) Variation of $T_{f'}$ for cooling/heating rate of 10 K/min as a function of the redox state for all investigated melts. Dotted lines in (a) and (b) are intended as a guide for the eye.

where ρ is the density; T, the temperature; and *a* and *b* are the fitting parameters, reported for each composition in Table 7. The density of the melts increases linearly with increasing iron content (Fig. 9), 30 wt.% of iron results in a maximum increase in density of 15%, with respect to the iron-free base composition. The density was calculated using the model of Lange and Carmichael (1987) by assuming (i) iron to be fully oxidised, (ii) to be fully reduced, and (iii) iron redox state as inferred by the model of Kress and Carmichael (1991) (Fig. 10). The discrepancy between the calculated and measured densities ranges between 0.1 and 0.7% within the investigated temperature intervals (Fig. 10). The density difference due to iron reduction is less than 1% (0.02 g·cm⁻³) for AD-5 and 5% (0.15 g·cm⁻³) for AD-30.

4. Discussion

4.1. Structure-property relations affecting viscosity

One model for describing the viscous behaviour of silicate melts is based on the configurational rearrangement of the melt structure with temperature (e.g. Richet, 1984). The Adam–Gibbs theory (Adam and Gibbs, 1965) is commonly used to describe the temperature dependence of silicate melt viscosity as a function of the configurational



Fig. 7. Viscosity calculated at T_f using Eq. (2) for the melts equilibrated in air (circles), and the most reduced samples (square). The errors bars are the maximum error of 0.3 log Pa s. The full lines represent the TVF fit for the melts equilibrated in air and the dashed lines for the reduced samples. Data from micropenetration are also plotted as small circles.

Table 6				
Density derived from buoyancy n	neasurements at high temperature	e for each investigated melts	with associated	standard deviation.

T (K)	Density (g·cm ³)									
	AD	St. dev	AD-5	St. dev	AD-10	St. dev	AD-20	St. dev	AD-30	St. dev
1840	2.591	0.010	2.643	0.011	2.696	0.005	2.809	0.006	2.977	0.046
1793	2.595	0.004	2.657	0.012	2.704	0.004	2.813	0.007	2.979	0.047
1746	2.602	0.006	2.663	0.012	2.712	0.003	2.819	0.007	2.989	0.049
1696	2.614	0.008	2.671	0.010	2.72	0.005	2.828	0.006	2.999	0.051
1639	2.617	0.012	2.671	0.003	2.732	0.007	2.837	0.006	3.003	0.059
1594	2.627	0.005	2.685	0.005	2.743	0.006	2.844	0.007	-	-
1542	2.63	0.006	2.695	0.007	2.751	0.007	2.855	0.009	-	-
1496	2.648	0.007	2.697	0.010	2.76	0.005	-	-	-	-
1473	-	-	-	-	2.766	0.009	-	-	-	-

entropy (e.g. Neuville and Richet, 1991; Richet and Bottinga, 1995; Sipp et al., 1997; Toplis et al., 1997; Romano et al., 2003) via:

$$\log \eta = A_{\rm AG} + \frac{B_{\rm AG}}{T \cdot S^{\rm C}} \tag{5}$$

where AAG is a pre-exponential factor equivalent to a lower limit of silicate melt viscosity at high temperature; BAG the activation energy; and S^C, the configurational entropy of the liquid. A_{AG} is a constant independent of temperature and composition (Russell et al., 2003; Giordano and Russell, 2007) whereas BAG is dependent upon composition and S^C is both temperature and compositionally dependent (Toplis, 1998). This theory represents a reliable way to incorporate the viscosity data into a model, since the theoretical basis outlined here allows confident extrapolation beyond the range of conditions of the viscosity measurements. As discussed in previous contributions (e.g., Richet and Neuville, 1992; Toplis et al., 1997; Giordano et al., 2009), S^C can be expressed as the sum of two competing bonding mechanisms, namely the "topological" and the "chemical" contributions. The "topological" contribution is referred to the distribution of the bonding angles and lengths at the short- and intermediate-range order in the oxygen lattice of the silicate network (e.g. Henderson, 2005; Stebbins, 2008). On the other hand, the "chemical" contribution is a reflection of the ability of various cations, competing with their neighbourhoods, to adopt new configurations. This contribution is proportional to the degree of polymerisation, and to the viscosity of silicate melts (Giordano et al., 2009). To represent the degree of polymerisation, the ratio of non bridging oxygens per tetrahedrally coordinated cations, NBO/T (Mysen, 1988) or, as suggested by Giordano and Dingwell (2003a), the sum of structure



Fig. 8. Density of the investigated melts vs. temperature. The errors bars are the standard deviation based on replicate buoyancy determinations. The triangles are the density measurements from Holzapfel et al. (2001) for anorthite–diopside eutectic composition.

modifiers (SM parameter) can be used. Here, both parameters are calculated on the basis of the measured iron redox ratio considering Fe³ as a network former and Fe^{2+} as network modifier (Mysen et al., 1984) and are reported in Table 3. For a given redox state, the depolymerisation is therefore directly proportional to iron content. Treating the investigated melts as pseudo-binary mixtures between iron-free and iron-bearing AD component, the variation of ΔH_n in Fig. 5 represents the activation energy of mixing due to the addition of total iron, hence decreasing polymerisation. At low-T, the non-linearity of ΔH_n indicates significant "chemical" interactions between the components of the mixture. This observation is strongly supported by previous studies on silicate melts (e.g. Neuville and Richet, 1991; Toplis et al., 1997) and has been recently extended for a large body of anhydrous and hydrous natural multicomponent melts by Giordano et al. (2009). A comparison with this latter study is shown in Fig. 11 where the isothermal viscosity variation of natural multicomponent melts is plotted as a function of the SM parameter. Up to SM~33 mol% the viscosity of multicomponent melts follows a monotonous path of decrease with the SM parameter. The viscosity distribution becomes gradually more scattered and curved towards the lower temperatures where chemical interactions are more significant. At the lowest temperature (1070 K), the isothermal viscosity variation for the samples measured in this work (SM > 40 mol%) show a marked contrast with the overall trend. The discrepancy is stronger for the pure AD sample (higher viscosity) and tends to vanish as iron is added to the AD melt. This observation demonstrates that a simplified melt such as the AD-eutectic does not follow the overall viscosity trend of natural multicomponent melts. On the other hand, it appears that the dissolution of a certain amount of iron is of critical importance to reduce the chemical interaction between the cations in the AD-eutectic system and yields the overall trend of multicomponent melts for these compositions. Furthermore, the fragility values indicate that iron enhances the non-Arrhenian behaviour of the melt consistent with the observation that iron-rich silicate melts are poor glassformers, like natural basaltic compositions.

4.2. Effect of redox state

At high temperature, investigation of the effect of iron redox on viscosity reveals a slight viscosity decrease as the melt is reduced.

Linear fit parameters of the temperature dependence of density using Eq. (4).									
Sample	a	10 ⁴ b	RMSE ^a						
AD	2.875	- 1.558	0.004						
AD Holzapfel et al., 2001	2.891	-1.604	0.003						
AD-5	2.925	-1.514	0.004						
AD-10	3.042	-1.888	0.001						
AD-20	3.078	-1.473	0.002						
AD-30	3.240	-1.439	0.003						

^a Root mean square error.



Fig. 9. Effect of iron expressed as the bulk molar fraction of Fe_2O_3 on the isothermal density. The ordinate axis is the percentage change with respect to an iron-free anor-thite-diopside eutectic composition.

This viscosity decrease is in the same order of magnitude as previous observations on basaltic compositions (Bouhifd et al., 2004). However, for other compositions, the redox effect was observed to be stronger (Dingwell and Virgo, 1987). This difference may be attributed to 1) the lack of highly oxidised melt compositions in this study; 2) the fact that ferric and ferrous iron may have similar structural roles in the present melts at very high temperatures or 3) the presence of alkaline earths (e.g., Mg and Ca), which render the effect of iron on the melt structure less effective with respect to alkalies (Dingwell and Virgo, 1987, 1988; Dingwell, 1991; Toplis et al., 1994). Although the viscosity decrease is small, the non-linear trend is consistent with the observations of Dingwell (1991). Near the glass transition temperature the viscosity is more sensitive to the redox state. For AD-20, a decrease of 1 log unit is observed between the sample equilibrated in air (Fe^{2+}) $Fe_{tot} = 0.18$) and the most reduced sample ($Fe^{2+}/Fe_{tot} = 0.67$). The non-linear decrease of the calorimetric limiting T_f' with reduction of the melts leads to analogous behaviour for the calculated viscosity. As in the high temperature range, the viscosity decreases with iron reduction until a minimum value is reached around $Fe^{2+}/Fe_{tot} = 0.5$ and then remains constant with further reduction. This observation is consistent with the previous study of Cukierman and Uhlmann (1974) on lunar iron-rich basalt. In their study, melt reduction (from $Fe^{2+}/Fe_{tot} =$ 0.2 to 0.76) involved a viscosity decrease of two orders of magnitude whereas further reduction ($Fe^{2+}/Fe_{tot}=0.94$) yielded no further viscosity change. Liebske et al. (2003) also found in experiments on andesite compositions that, in the same way, viscosity decreases non-linearly with iron reduction; the difference between the oxidised $(Fe^{2+}/Fe_{tot}=0.42)$; and the reduced sample $(Fe^{2+}/Fe_{tot}=0.79)$ was 1.6 log units at 1061 K. Consequently, we recommend that future studies incorporate iron redox state in multicomponent viscosity models applicable to natural systems. The decrease of viscosity with reduction of iron that is correlated to an increase of depolymerisation suggests that Fe³⁺ acts as network former while Fe²⁺ acts as network modifier. In contrast, the invariant viscosity after further reduction than $Fe^{2+}/$ $Fe_{tot} = 0.5$ hints that iron may develop differents coordination state at low fO2. Mysen, 1991 suggested that an octahedral coordination is preferred by ferric iron under reducing conditions.

4.3. Experimental limitation for oxidised iron-rich melts

The calorimetric measurements for the sample AD-20-S1 ($Fe^{2+}/Fe_{tot} = 0.18$) that was equilibrated in air were experimentally challenging. For the same heating/cooling rate the cycles were not reproducible. As soon as the glass transition peak was overcome the heat capacity curve shows an exothermal peak and the calorimetric liquid field could never be reached. Even if the heating is stopped as soon as the

peak is reached, the next cycle with the same heating/cooling rate shows a shift toward higher temperatures. In contrast, samples equilibrated in reduced conditions are more "stable" through the glass transition until the liquid field and measurements were reproducible by crossing the glass transition back and forth. As shown by Bouhifd et al. (2004), crystal nucleation strongly increases with increase of iron content and iron oxidation. Although no crystals are visible with Secondary Electron Microprobe images, we suspect that nano-crystals could be evidenced within the oxidised sample using transmission electron microscopy (Liebske et al., 2003; Bouhifd et al., 2004). The shift of Tg toward higher values is in agreement with the possible crystallisation, as the matrix would evolve toward higher silica content and hence higher T_g . The T_{f^\prime} value presented here for AD-20-S1 are therefore the best that could be obtained, but should be treated with caution. The properties of iron-rich melts near Tg must be investigated with care for oxidised sample, avoiding nano-crystallisation.

4.4. Iron-rich melt densities

Another factor controlling magma dynamics is melt density. The model of Lange and Carmichael (1987) reproduces the high temperature-dependence of density observed here, very well. The measurements performed in this study reveal that density increases proportionally with iron concentration, 10 mol% of iron yields a 10% density increase (Fig. 9). The variation of density with redox state is obviously related to the iron content. According to the model of Lange and Carmichael (1987), the maximum variation between fully oxidised and fully reduced is estimated at 5% for AD-30. However it is important to note that 1) the uncertainties on the measurements of such iron-rich melt are high (4 to 5%) and 2) the model does not consider melts with such high iron contents. Therefore this estimation is qualitative at best. A more reasonable estimation for the effect of iron redox state on the density of iron-rich basalts may lie between the results from AD-10 and AD-20 compositions as those melts are better analogues for natural material. Therefore, at magmatic temperature (1470 K), the density of a natural iron-rich undersaturated basaltic melt may be expected to be between $2.76 \pm 1.5\%$ and $2.86 \pm$ $3\% g \cdot cm^{-3}$. These values are in agreement with the estimation for komatiitic lava (Lange and Carmichael, 1987).

4.5. Applications to extra-terrestrial magmatism

Fig. 12 displays a comparison of the viscosity measured in this study with data available in the literature on undersaturated iron-rich natural compositions from the Earth (Kushiro et al., 1976; Toplis et al., 1994; Gottsmann et al., 2002; Giordano and Dingwell, 2003b; Bouhifd et al., 2004) and from the Moon (Murase and McBirney, 1970; Cukierman et al., 1973; Uhlmann et al., 1974). Iron-bearing AD melts cover the same viscosity range, and have similar patterns, to those observed for terrestrial and extra-terrestrial melts. Giordano et al. (2008b) showed that anorthite-diopside eutectic melt cannot be used as quantitative analogue for calculating the viscosity of Etna basalt because of the differing fragilities of the two melts. However, here we show that iron significantly lowers the activation energy of viscous flow at low temperature and brings the iron-bearing anorthite-diopside system closer to approximate the behaviour of natural multicomponent melts. Iron is therefore a requirement in the construction of a basaltic equivalent for terrestrial and extra-terrestrial magmas. Based on our results on iron-bearing anorthite-diopside, the difference in viscosity at magmatic temperatures between AD-10, analogous to 'common' terrestrial basalts (with 10 wt.% Fe_2O_{3tot}) and AD-20, analogous to lunar or Martian basalt (with 20 wt.% Fe₂O_{3tot}), is estimated to be between 0.5 and 1 order of magnitude. This belief is consistent with the experimental investigation of lunar basalt viscosity displayed in Fig. 12. The predicted low viscosities are also coherent with morphological interpretation of



Fig. 10. Measured (symbols) vs. calculated (bold lines) 1-bar density. Thin black lines are linear fit of the data (Table 7). Calculations were carried out with the model of Lange and Carmichael (1987) for fully reduced (grey full line) and fully oxidised (dotted grey line) liquids.

lava flow on the Moon and on Mars (Huppert and Sparks, 1985; Cas et al., 1999; Baratoux et al., 2009; Hauber et al., 2009; Vaucher et al., 2009). The low viscosity calculated in Vaucher et al. (2009) for



Fig. 11. Isothermal viscosity curves as a function of the SM parameter approximating the degree of polymerisation. Numbers in the figures are isotherm temperatures and are the same for all panels. The full symbols are from previous study (Giordano et al., 2009) and empty symbols from this study.

young lava flows in Central Elysium Planitia province on Mars could partly be explained by high iron content. Although no chemical data are available on this area, the nearest volcanic province, Elysium Mons contains the highest iron content observed on Mars (21-22 wt.%). Furthermore iron-rich basalt has a high liquidus temperature and this implies that during eruption a solid crust would form rapidly, forming tubes and allowing the lava to travel very long distances. However, it is important to highlight that the relationship between the viscosity of extruded lava and the final morphology of a flow is not yet well defined. The lava flow behaviour depends more on the crystallisation sequence than on the pure melt viscosity. The crystallisation sequence of such iron-rich basalt needs further attention in order to draw solid conclusions on the quantitative behaviour of extraterrestrial lava flows. Finally, Baratoux et al. (2011) show that the magmatic evolution on Mars follows a simple model of mantle convection with a lithosphere thickening. As the source of the magma deepens (150 km), the high-iron content of such a melt would favour the efficient transport of the material through the crust to reach the surface.

5. Conclusion

This is the first systematic study of the physical and thermodynamic properties of iron-bearing anorthite–diopside-eutectic melts as a proxy for extra-terrestrial magmas. Our investigation shows that viscosities of the investigated analogue melts match the



Fig. 12. Viscosity of basaltic melts experimentally determined, comparison between this study (circles) and terrestrial (square) and lunar (triangles) data. Terrestrial compositions include trachy-basalt from Etna (Giordano and Dingwell, 2003b), ferro-basalt (Toplis et al., 1994), basalt from Hawaii (Kushiro et al., 1976 and R839-5.8, Gottsmann et al., 2002) and basalt from Stein Frentz (Bouhifd et al., 2004). Lunar compositions include Ti-rich basalt from Apollo 11 (Murase and McBirney, 1970), green glass basaltic (Cukierman and Uhlmann, 1974).

viscosities of natural terrestrial and extra-terrestrial basalts well. We outline here that iron can dramatically affect viscosity, glass transition temperatures and density. The addition of 20 wt% of iron to the anorthite–diopside eutectic composition produces: 1) a significant absolute viscosity decrease of up to 2 log units near the glass transition and, 1 log unit at magmatic temperature; 2) an increase of density by 10%. The iron-rich basaltic compositions such as those found on the Moon or on Mars should have, at eruption temperature, lower viscosity and should be slightly denser than 'common' terrestrial basalts. To conclude, the low viscosity of iron-bearing melts would enhance the transport distance of magma travelling through the crust and / or at the surface, however the crystallisation sequence should be investigated to draw quantitative conclusions on extra-terrestrial lava flow behaviour.

The investigation of the effect of iron redox state is consistent with previous studies that also observed a viscosity decrease with reduction of iron. Iron speciation appears to influence viscosity strongly above a certain concentration and near Tg. From calorimetric measurements we infer that there is a threshold at $Fe^{2+}/Fe_{tot} = 0.5$ beyond which the glass transition temperature ceases decreasing and viscosity becomes constant. The reduced supercooled melts are more 'stable' through the glass transition and show lower fragility than oxidised melts. Care should be taken when oxidised iron-rich melt (equilibrated in air) are analysed near the glass transition. The density is also affected by the redox state of iron only for iron-rich melts and should not exceed more than 3% variation for natural iron-rich melts. To conclude, for basaltic magmas that contain high iron concentration (above 10 wt.%), the redox state must be determined in order to obtain more accurate estimation of the physical and thermodynamic properties, especially at low temperatures.

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