

High-pressure aragonite phenocrysts in carbonatite and carbonated syenite xenoliths within an alkali basalt

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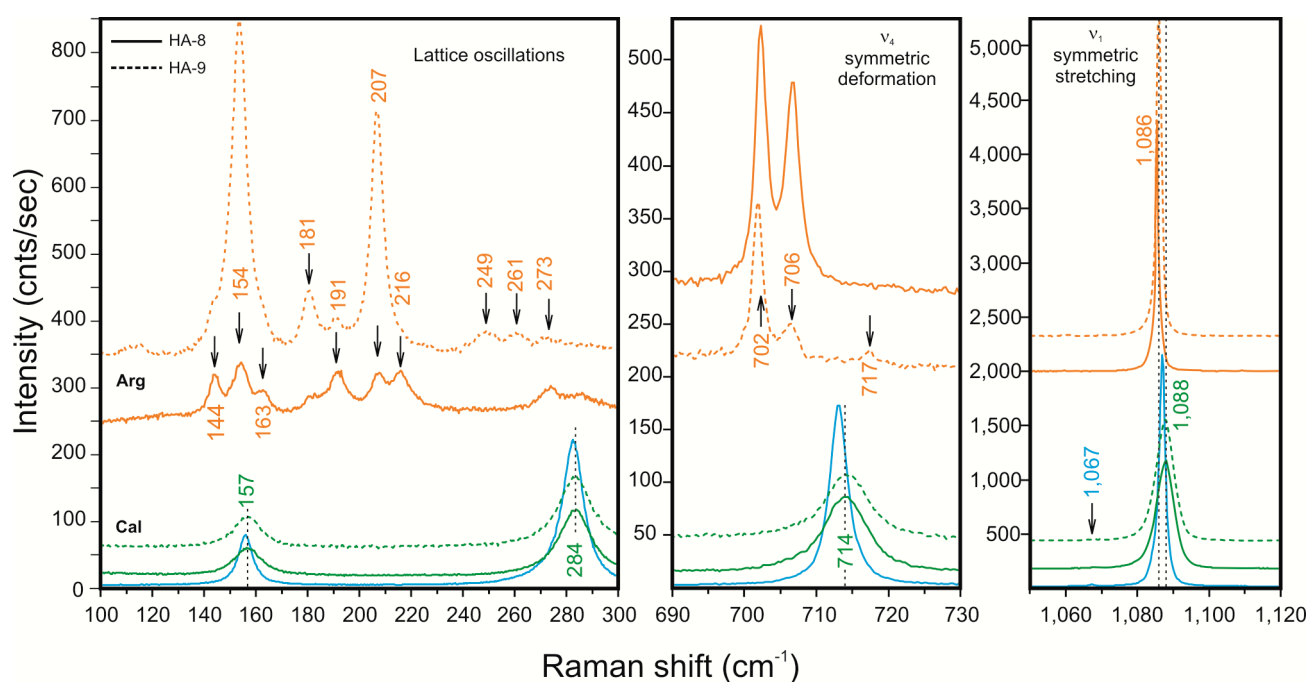
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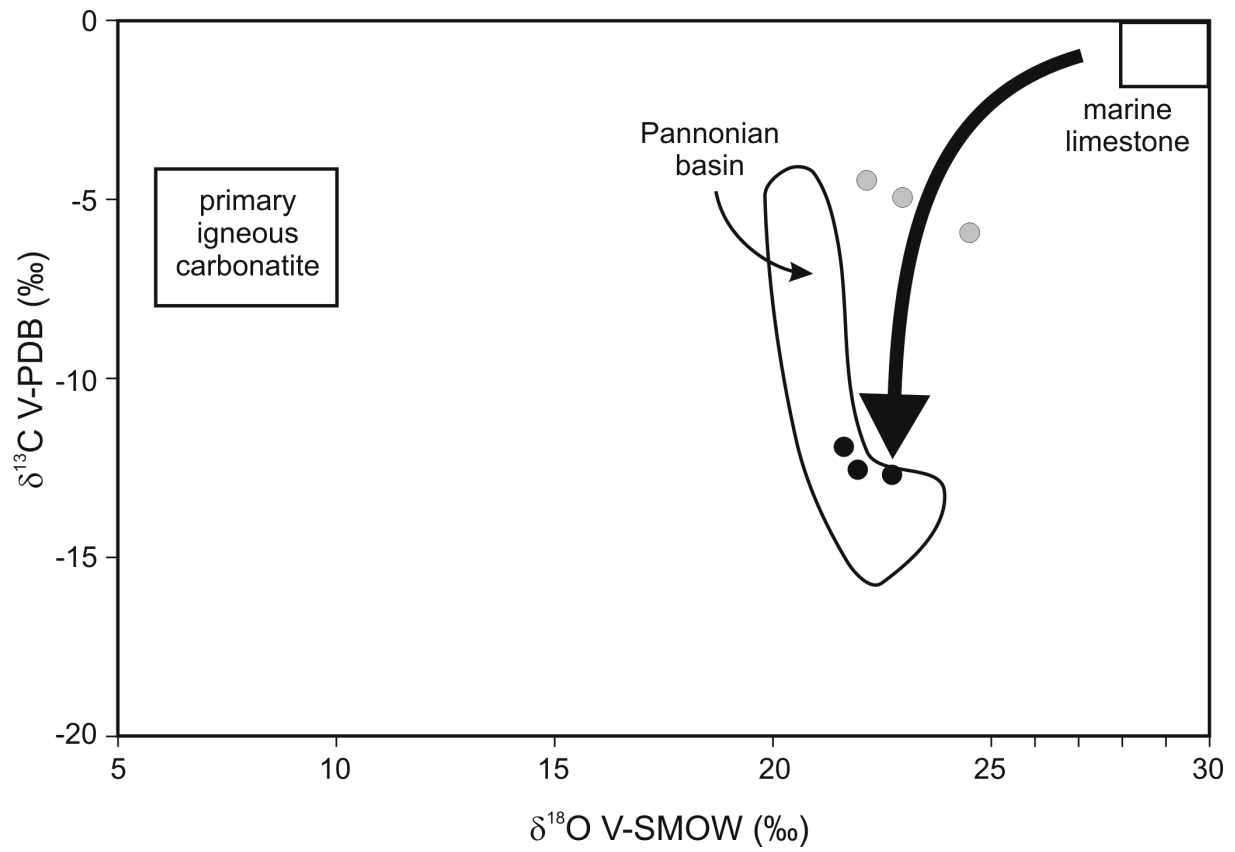
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1. Supplementary Figures



Supplementary Figure 1. High-resolution (0.33 cm/pixel) Raman spectra of aragonite (orange), calcite matrix (green) and reference low-temperature hydrothermal calcite (blue).



Supplementary Figure 2. Carbon and oxygen isotope compositions of aragonite (grey circles) and calcite (solid circles) from carbonatite HA-9 (this work), calcite from metasomatised mantle xenoliths of Pannonian alkali basalts, marine limestone (Demény et al. 2004, 2010), and primary igneous carbonatites (Keller and Zaitsev 2006). Thick curve designates approximate devolatilization trend.

2. Supplementary Tables

Supplementary Table 1. Representative electron microprobe analyses (wt% oxides).

Sample	HA-8					HA-9			
Xenolith	Carbonated syenite					Carbonatite			
Phase	Si-glass	Calcite	Calcite	Aragonite	Aragonite	Calcite	Calcite	Aragonite	Aragonite
P ₂ O ₅	0.06	0.29	0.05	0.08	0.13	0.20	0.32	bdl	0.05
SiO ₂	62.38	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Al ₂ O ₃	15.98	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
FeO [*]	3.45	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
MnO	0.28	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
MgO	0.48	1.45	2.93	bdl	bdl	2.21	0.87	bdl	bdl
CaO	1.80	54.62	52.43	55.02	55.41	53.80	54.33	54.24	55.66
SrO	bdl	bdl	bdl	0.72	1.03	bdl	bdl	1.80	0.69
BaO	0.13	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.06
Na ₂ O	5.30	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
K ₂ O	6.59	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
CO ₂ [†]		44.15	44.29	43.40	43.79	44.43	43.26	43.33	43.94
Total	96.45	100.51	99.70	99.22	100.36	100.64	98.78	99.37	100.40

Notes:

As, S, Ti, Y, La, Ce, Pr, Nd, Cl and F are all below detection limits – bdl

^{*} iron measured as FeO

[†] calculated assuming molar proportion of Ca = $3.333 \times P$ in normative apatite and the remaining cations as carbonate

Supplementary Table 2. Statistical parameters of deconvoluted Raman spectra of calcite and aragonite**Aragonite**

HA-8						HA-9						Assignment
Center (cm ⁻¹)	StdErr	FWHM (cm ⁻¹)	Area	Amplitude (cnts)	I/I ₀	Center (cm ⁻¹)	StdErr	FWHM (cm ⁻¹)	Area	Amplitude (cnts)	I/I ₀	
144.1	0.0	5.0	9,038	1,162	0.020							A _g
154.1	0.0	7.2	13,051	1,435	0.024	153.6	0.0	6.3	81,502	9,212	0.208	B _{1g}
						159.5	0.9	9.5	11,346	900	0.020	A _g ?
162.8	0.1	5.7	4,511	597	0.010							A _g
182.2	0.6	8.4	4,110	423	0.007	180.6	0.1	6.2	11,406	1,587	0.036	B _{2g} /B _{3g}
191.5	0.2	7.0	9,679	1,089	0.019	190.7	0.2	7.2	7,249	726	0.016	B _{3g} /A _g
207.3	0.2	6.5	8,848	985	0.017	206.8	0.1	5.0	47,335	6,371	0.144	B _{2g}
215.6	0.3	7.5	9,907	966	0.016							A _g
273.5	0.7	8.8	6,727	571	0.010	274.2	1.3	16.0	7,599	302	0.007	B _{3g}
702.3	0.0	1.8	13,221	4,765	0.081	701.9	0.0	1.7	7,913	3,042	0.069	B _{3g}
706.7	0.0	2.3	13,633	3,743	0.064	706.4	0.0	2.4	1,686	596	0.013	A _g
					0.000	717.3	0.1	1.7	549	228	0.005	B _{2g}
					0.000	853.6	0.2	2.2	384	130	0.003	A _g /B _{3u} TO
1,060.2	1.0	2.3	374	154	0.003	1,059.8	0.8	1.7	276	108	0.002	v ₁ C ¹⁸ O ¹⁶ O ₂
1,083.5	0.3	2.6	9,434	2,331	0.040	1,084.2	1.2	2.5	6,000	1,719	0.039	B _{3u} TO
1,085.9	0.0	1.7	127,600	58,806	1.000	1,085.4	0.0	1.2	76,899	44,192	1.000	A _g /B _{1u} TO
1,463.6	0.2	3.6	724	128	0.002	1,462.1	0.2	5.0	1,416	182	0.004	A _g /B _{1u} TO

Calcite

HA-8						HA-9						Assignment
Center (cm ⁻¹)	StdErr	FWHM (cm ⁻¹)	Area	Amplitude (cnts)	I/I ₀	Center (cm ⁻¹)	StdErr	FWHM (cm ⁻¹)	Area	Amplitude (cnts)	I/I ₀	
156.7	0.0	13.0	16,356	901	0.046	156.8	0.1	13.0	9,395	700	0.032	E _g
283.4	0.0	15.0	49,700	2,083	0.107	283.4	0.0	15.0	40,233	1,891	0.087	E _g
714.3	0.0	6.9	10,766	1,179	0.061	714.0	0.0	7.1	13,049	1,400	0.064	E _g
1,068.5	0.3	4.4	700	101	0.005	1,068.2	0.3	5.8	1,097	121	0.006	v ₁ C ¹⁸ O ¹⁶ O ₂
1,087.9	0.0	5.6	134,750	19,394	1.000	1,087.8	0.0	5.7	152,100	21,852	1.000	A _{1g}
1,438.0	0.2	11.0	2,386	144	0.007	1,438.1	0.1	9.5	2,237	151	0.007	E _g

Notes:

FWHM – full-width-at-half-maximum

Peak assignment according to [Schauble et al. \(2006\)](#)

3. Methods

Mineral and glass compositions were measured using a CAMECA SX-100 electron microprobe (Geological Survey of Slovakia, Bratislava) calibrated against natural and synthetic minerals (average detection limits in ppm in parentheses): Na (650) – albite, Si (350) and K (230) – orthoclase, Ca (300) – wollastonite, P (300) – apatite, Fe (650) – fayalite, Al (330) – Al_2O_3 , S (220) and Ba (530) – barite, Sr (700) – SrTiO_3 , Mg (450) – forsterite, Mn (630) – rhodonite, Cl (200) – NaCl, F (1000) – LiF, Y (500) – YPO_4 , La (670) – LaPO_4 , Ce (600) – CePO_4 , Pr (620) – PrPO_4 , Nd (570) – NdPO_4 , As (300) – GaAs, Ti (600) – TiO_2 . Counts were measured at 15 kV accelerating voltage, 20 nA beam current, and 5 μm beam diameter. An extended beam diameter of 20 μm was used for silicate glass. Raw analyses were recalculated to weight percents of oxides using a standardized PAP correction (Pouchou and Pichoir 1984).

Raman spectra and maps were recorded with a Horiba Jobin-Yvon LabRam HR800 spectrometer with 1800 gr/mm (point analyses) and 600 gr/mm (maps) gratings equipped with an Olympus BX-41 optical microscope. Samples were illuminated with a 633 nm, 17 mW LHX1 CVI Melles Griot He-Ne laser. A long-working-distance LMPLanFI 100 \times 0.8 objective was used to focus the laser beam and to collect the scattered light with a Peltier-cooled (-70 °C), multichannel Synapse CCD detector (1024 \times 256 pixels) at spectral resolutions 1.2 and 0.33 cm per pixel depending on the grating used. Positions of the Raman bands were controlled using the principal line of silica at 520.7 cm^{-1} . Deconvolution of the Raman spectra and the peak identification was made using PeakFit® program from Seasolve Software, Inc.

Stable C and O isotope analyses of carbonates were performed using an automated gasbench device with carbonate option (Thermo Scientific) following the acid digestion method (McCrea 1950). Samples of finely ground carbonate, 50-100 μg in weight, were loaded into borosilicate glass vials (Labco), sealed with septum, and flushed with helium at 72 °C to remove atmospheric gases. Subsequently, a total of 5 drops of anhydrous phosphoric acid were injected, and evolved CO_2 gas was carried in helium stream through Nafion (TM) water trap into sample loop and repetitively passed onto an isothermal GC column (70 °C). Series of eight eluting CO_2 pulses preceded by three pulses of reference gas were delivered via an open split to the ion source of a MAT253 (Thermo Scientific) mass spectrometer operating in continuous-flow regime. Uncertainty of the sample measurements bracketed by 4 analyses of working standard (ATC-1) was within ± 0.5 ‰ for carbon and ± 0.6 ‰ for oxygen.

4. Supplementary references

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