

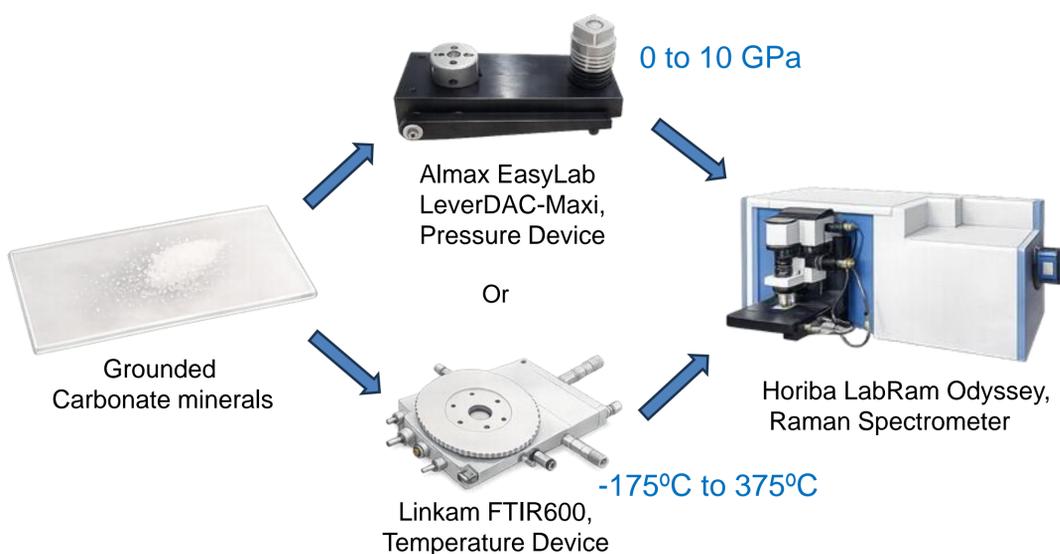
Raman spectroscopy for determining thermodynamic properties of carbonate minerals

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INTRODUCTION & AIM

Carbonate minerals occur in great abundance in the Earth's crust, with calcite (CaCO₃) being the most widespread representative. These minerals are classified into four structural groups: calcite, dolomite, aragonite, and hydroxyl-bearing carbonate groups. Members of the calcite and dolomite groups crystallize in the rhombohedral system, whereas aragonite adopts an orthorhombic structure, and hydroxyl-bearing carbonates are characterized by monoclinic symmetry. Carbonates play a crucial role in the global carbon cycle, serving as major carriers of carbon into the deep Earth. Consequently, the investigation of their physicochemical properties under high-pressure and high-temperature conditions is of considerable scientific interest. Raman spectroscopy is widely employed to obtain thermodynamic properties of these materials because the vibrational properties of a mineral control several of its thermodynamic properties.

METHOD



RESULTS & DISCUSSION

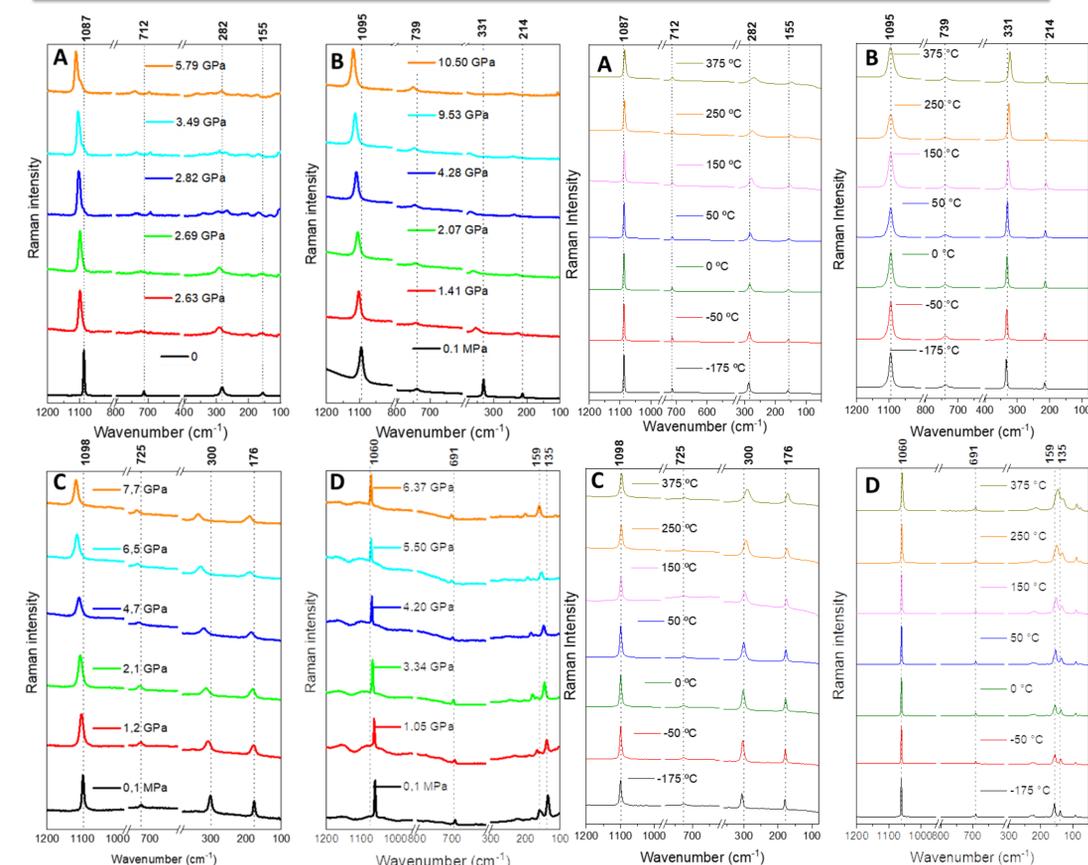


Figure 1. Raman spectra of the carbonates at varying compression pressures, ranging from 100 to 1200 cm⁻¹, using the lasers at 633 nm and 532 nm (only for Witherite mineral) as excitation source. (A) Calcite. (B) Magnesite. (C) Dolomite. (D) Witherite.

Figure 2. Raman spectra of the carbonates at varying temperatures, ranging from 100 to 1200 cm⁻¹, using the laser at 532 nm as the excitation source. (A) Calcite. (B) Magnesite. (C) Dolomite. (D) Witherite.

↑ Pressure ↑ Maximum band intensities shift to higher wavenumbers
 ↑ Temperature ↓ Maximum band intensities shift to lower wavenumbers

Grüneisen Parameters

$$\gamma_T = \frac{1}{\alpha v_i} \left(\frac{\partial v_i}{\partial T} \right)_P$$

$$\gamma_T = \frac{-K_t}{v_i} \left(\frac{\partial v_i}{\partial P} \right)_T$$

$$a_i = \alpha(\gamma_T - \gamma_P)$$

γ_T = Isothermal Grüneisen parameter
 γ_P = Isobaric Grüneisen parameter
 v_i = Vibrational frequency at ambient conditions
 α = Thermal expansion coefficient
 K_t = Bulk modulus
 T = Temperatura
 P = Pressure

| Calcite | | | | | | Literature[1] | | |
|---------------------------|--|--|------------|------------|---|---------------|------------|---|
| v_i (cm ⁻¹) | $\left(\frac{\partial v_i}{\partial T}\right)_P$ (cm ⁻¹ K ⁻¹) | $\left(\frac{\partial v_i}{\partial P}\right)_T$ (cm ⁻¹ GPa ⁻¹) | γ_P | γ_T | $\left(\frac{a_i}{10^{-5} \text{ K}^{-1}}\right)$ | γ_P | γ_T | $\left(\frac{a_i}{10^{-5} \text{ K}^{-1}}\right)$ |
| 1087 | -0.0046 | 4.19 | 0.47 | 0.28 | -0.17 | 0.51 | 0.40 | -0.1 |
| 713 | -0.0016 | 2.24 | 0.25 | 0.23 | -0.021 | 0.62 | 0.23 | -0.3 |
| 287 | -0.031 | 3.12 | 11.86 | 0.81 | -9.95 | 15.8 | 1.4 | -13.0 |
| 159,5 | -0.022 | 2.16 | 15.30 | 1.01 | -12.86 | 19,9 | 1.2 | -16.9 |
| Magnesite | | | | | | Literature[1] | | |
| v_i (cm ⁻¹) | $\left(\frac{\partial v_i}{\partial T}\right)_P$ (cm ⁻¹ K ⁻¹) | $\left(\frac{\partial v_i}{\partial P}\right)_T$ (cm ⁻¹ GPa ⁻¹) | γ_P | γ_T | $\left(\frac{a_i}{10^{-5} \text{ K}^{-1}}\right)$ | γ_P | γ_T | $\left(\frac{a_i}{10^{-5} \text{ K}^{-1}}\right)$ |
| 1095,5 | 0.000013 | 1.43 | -0.00062 | 0.16 | 0.31 | 0.17 | 0.28 | 0.21 |
| 738 | 0.0030 | 0.786 | -0.21 | 0.13 | 0.65 | 0 | 0.23 | 0.44 |
| 334 | -0.021 | 2.82 | 3.26 | 1.04 | -4.28 | 3.0 | 1.7 | -2.5 |
| 216 | -0.014 | 2.13 | 3.41 | 1.21 | -4.23 | 2.4 | 2.6 | 0.3 |
| Dolomite | | | | | | Literature[1] | | |
| v_i (cm ⁻¹) | $\left(\frac{\partial v_i}{\partial T}\right)_P$ (cm ⁻¹ K ⁻¹) | $\left(\frac{\partial v_i}{\partial P}\right)_T$ (cm ⁻¹ GPa ⁻¹) | γ_P | γ_T | $\left(\frac{a_i}{10^{-5} \text{ K}^{-1}}\right)$ | γ_P | γ_T | $\left(\frac{a_i}{10^{-5} \text{ K}^{-1}}\right)$ |
| 1098 | -0.0057 | 2.51 | 0.21 | 0.216 | 0.0040 | 0.24 | 0.25 | 0.0 |
| 726 | -0.0044 | 1.72 | 0.25 | 0.22 | -0.061 | 0.12 | 0.2 | 0,2 |
| 301,5 | -0.031 | 4.00 | 4.22 | 1.38 | -6.83 | 4.4 | 1.4 | -7.3 |
| 177,5 | -0.016 | 1.86 | 3.64 | 0.99 | -6.39 | 4.4 | 0.9 | -8.5 |
| Witherite | | | | | | Literature[2] | | |
| v_i (cm ⁻¹) | $\left(\frac{\partial v_i}{\partial T}\right)_P$ (cm ⁻¹ K ⁻¹) | $\left(\frac{\partial v_i}{\partial P}\right)_T$ (cm ⁻¹ GPa ⁻¹) | γ_P | γ_T | $\left(\frac{a_i}{10^{-5} \text{ K}^{-1}}\right)$ | γ_P | γ_T | $\left(\frac{a_i}{10^{-5} \text{ K}^{-1}}\right)$ |
| 1060,5 | -0.0047 | 1.85 | 0.069 | 0.10 | 0.022 | 0.20 | 0.15 | -0.33 |
| 690 | 0.00085 | 1.57 | -0.019 | 0.13 | 0.099 | 0.05 | 0.12 | 0.46 |
| 157,5 | -0.020 | 6.14 | 1.95 | 2.27 | 0.20 | 2.06 | 1.28 | -5.07 |
| 139,5 | -0.016 | 3.45 | 1.82 | 1.50 | -0.21 | 2.38 | 1.37 | -6.57 |

Table 1. Variation of wavenumber with pressure and temperature; isobaric and isothermic grüneisen parameters; anharmonicity for calcite, magnesite, dolomite and witherite minerals.

CONCLUSION

- ✓ Four carbonate minerals were analyzed through Raman spectroscopy and had their **thermodynamic properties determined**.
- ✓ Values of the **isobaric and isothermal Grüneisen parameters** were determined, as well as **anharmonicity parameters** for each of these minerals.
- ✓ The fitting procedure used to obtain these properties included a linear model for **four different Raman modes of the minerals**. The results obtained are **promising and consistent** with previously reported literature data.

FUTURE WORK / REFERENCES

- Gillet, P.; Biellmann, C.; Reynard, B.; McMillan, P. Raman Spectroscopic Studies of Carbonates Part I: High-Pressure and High-Temperature Behaviour of Calcite, Magnesite, Dolomite and Aragonite. *Phys. Chem. Miner.* **1993**, *20*, 1–18, doi:10.1007/BF00202245.
- Wang, X.; Ye, Y.; Wu, X.; Smyth, J.R.; Yang, Y.; Zhang, Z.; Wang, Z. High-Temperature Raman and FTIR Study of Aragonite-Group Carbonates. *Phys. Chem. Miner.* **2019**, *46*, 51–62, doi:10.1007/s00269-018-0986-6.